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CONDENSATION OF SUPERSATURATED He⁴ VAPOR IN A CLOUD CHAMBER¹

M. H. EDWARDS AND W. C. WOODBURY

ABSTRACT

The critical supercooling, ΔT_c , required to produce visible condensation in pressure-limited adiabatic expansions of presumably ion-free saturated He⁴ vapor has been measured in a small glass cloud chamber. The transient gas temperatures were measured during expansions by using a carbon resistance thermometer in a Wheatstone bridge. An oscilloscope was used in place of a galvanometer, and its trace was photographed during expansions. Low-amplitude temperature oscillations in the gas, which might not normally have been detected, were frequently observed in the early stages of this work. These oscillations either appeared spontaneously ("Taconis Resonances"), or could be shock-excited by an expansion. These oscillations were subsequently eliminated. Condensation thresholds were then measured using starting temperatures from 4.2 to 1.7° K. ΔT_c dropped from about 50 to 60 mdeg above the λ point to less than 20 mdeg below the λ point. The critical supersaturations required to produce condensation were thus always less than 105%. The supersaturations were calculated without making the usual, but highly implausible, assumption that the expanding gas is ideal. Assuming that the condensation nuclei are embryonic droplets arising accidentally from density fluctuations in the supersaturated vapor, the critical droplet radius is found to be about 10^{-6} cm above 2.5° K, although the theoretical treatment here is not rigorous.

1. INTRODUCTION

The physical processes involved in the initiation of condensation from a supersaturated vapor are by no means clear. Most cloud chamber experiments have involved the use of some condensable vapor mixed with another 'carrier' gas which does not participate in the condensation. Both gases are always assumed to be ideal in attempts at theoretical analyses of the processes.

The authors undertook to examine condensation in a single-component system, using pure He⁴ at low temperatures. Furthermore, the measurements of supercooling and consequent calculations of supersaturations were made without using the totally implausible assumption that a vapor on the verge of condensation behaves as an ideal gas.

2. EXPERIMENTS

2.1 Apparatus and Method

The condensation cloud chamber used (Fig. 1) consisted of a glass chamber C of about 110 cm³ volume, which had an offset lower tip L. The chamber was

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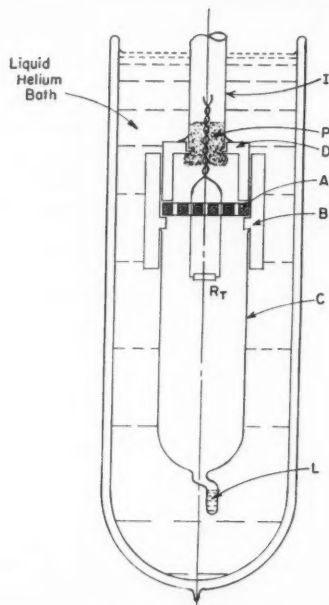


FIG. 1. The apparatus.

immersed in a liquid helium bath and connected to room temperature by a 5/8-in. outside diameter Inconel tube I, about 1 meter long, and then through a fast-acting Veeco solenoid vacuum valve (SV) to a large tank of approximately 24 liters volume. Tube I was soft-soldered into the brass top D of the chamber. The seal between D and C was effected by means of a Teflon bushing B, which was machined to be a press fit at room temperature. A light film of vacuum grease was wiped on the parts before each assembly. Upon cooling, the Teflon contracts so much more than either brass or glass that a seal tight to liquid helium II was regularly, but not invariably, formed. A bakelite spacer A was used to support the 56-ohm 1/2-w Allen Bradley carbon composition resistance thermometer R_T . Holes were drilled through A to permit easy gas flow past it. The leads to R_T were of No. 40 HF copper wire.

The cotton batten plug P was loosely stuffed into the lower end of I to eliminate temperature oscillations in the gas (see 2.2 later).

The chamber was illuminated by a 6-volt microscope illuminator used with three heat-absorbing filters. The chamber was viewed visually through the slits in the silvering of the liquid air and helium Dewars, in a darkened room. The helium clouds formed could best be seen when looking almost directly towards the light source.

A small amount of liquid L was condensed from an external filling system, into the offset tip of the cloud chamber, using He^4 gas which had been purified

by a liquid-air-cooled charcoal trap. The initial saturated vapor pressure, P_{1s} , in the chamber was then read and the SV closed. The large tank was adjusted to some pressure less than P_{1s} . Then the SV was opened so that an expansion to an essentially constant final pressure (the tank pressure) occurred. After a preset time, usually between 0.4 and 1.5 seconds, the SV was closed again. The cloud chamber was watched to determine whether or not a fog or cloud appeared in the supersaturated vapor. The temperature of the vapor was measured during expansions using the suspended carbon resistance thermometer R_T as one arm of a Wheatstone bridge. A medium persistence DuMont Type 403 oscilloscope with a d-c. sensitivity of $100 \mu\text{v}$ per cm was used in this bridge instead of a galvanometer. The drop in temperature ΔT of the vapor during expansion was recorded by photographing the oscilloscope trace. As the temperature fell the resistance R_T rose, and the bridge unbalanced, producing a deflection of the trace of the oscilloscope. This method of following the cooling during expansions was developed by Stachórska (1954, 1956). The power dissipated in R was kept below $1 \mu\text{w}$ and our sensitivity was then between 1 and $2 \times 10^{-3} \text{ }^\circ\text{K}$ per mm deflection of the oscilloscope trace.

Figure 2 shows a typical photograph of the oscilloscope trace, taken during an expansion from an initial temperature $T_1 = 2.725^\circ\text{K}$. The sweep speed was 250 milliseconds per division. The camera shutter was opened for a total of about 5 seconds showing parts of three sweeps. Starting near the upper right, the bridge was in balance. After about 1 second, the SV was opened (at about 1.8 divisions from left) and the temperature fell about 50 mdeg in about 100 milliseconds, and then remained nearly constant. After about 1.7

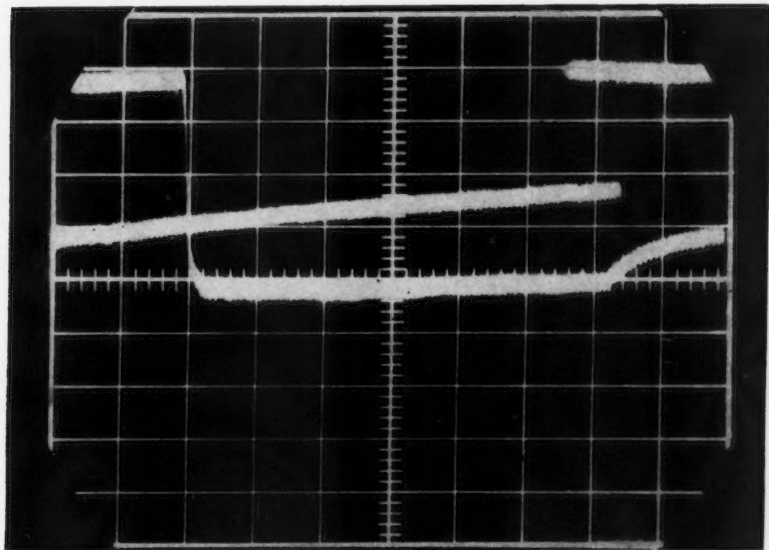


FIG. 2. Temperature record of a typical expansion.

seconds the SV was closed and the temperature began to rise towards the bath temperature. After a further 2.7 seconds, the shutter was closed again.

2.2 Temperature Oscillations in the Gas

(a) Spontaneous Oscillations

When the apparatus was first set up, without the cotton batten plug P (see Fig. 1) in place, low-amplitude temperature oscillations in the gas frequently occurred. Temperature oscillations in a gas column, one end of which is at room temperature, and the other at a low temperature, have been known to exist for many years (Keesom 1942) and are usually referred to as "Taconis resonances". The exact nature of the phenomenon is not clear (Taconis *et al.* 1949; Kramers 1949; ter Haar 1955). Audible resonances often are able to transport an impressive amount of heat (up to several watts) into a cryostat. Such large amplitude oscillations are very easy to detect when they occur because of the sound and/or the increased boil-off rate of the bath liquid.

The low-amplitude temperature oscillations which we observed might very easily have been overlooked without a cathode-ray oscilloscope in the bridge circuit of the resistance thermometer in the gas. Figure 3 shows such a low-amplitude resonance which occurred when the chamber was at a pressure of 21.5 mm Hg at 3.24° K (S.V.P. = 255.5 mm). The temperature amplitude is ± 22 mdeg at a frequency of 25 cycles/sec. At the same temperature with $P = 49.1$ mm Hg the amplitude was reduced to ± 12 mdeg, and above $P = 85$ mm Hg no resonance could be detected.

On some runs temperature oscillations occurred even at the saturated vapor pressure and below the λ point.

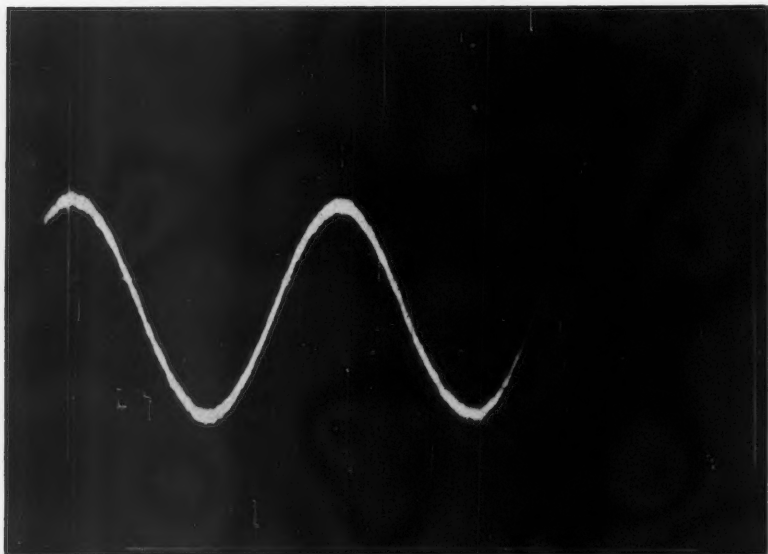


FIG. 3. Spontaneous temperature oscillation or "Taconis resonance".

Such oscillations, if undetected in apparatus of similar geometry in experiments to measure the He II film thickness or flow properties, might have very serious effects upon those measurements, because of the extreme sensitivity of such experiments to small temperature differences. It would be easy to install a carbon thermometer in a circuit such as we have described, in any film experiment. This could then act as a low-amplitude Taconis resonance detector.

(b) Shock-excited Oscillations

Even when we had chosen initial conditions for expansions where no temperature oscillations occurred, we regularly found that the expansion itself could excite a damped oscillation, as shown in Fig. 4, taken at 3.2° K with the SV kept open for 0.3 second. The frequency of this oscillation was about

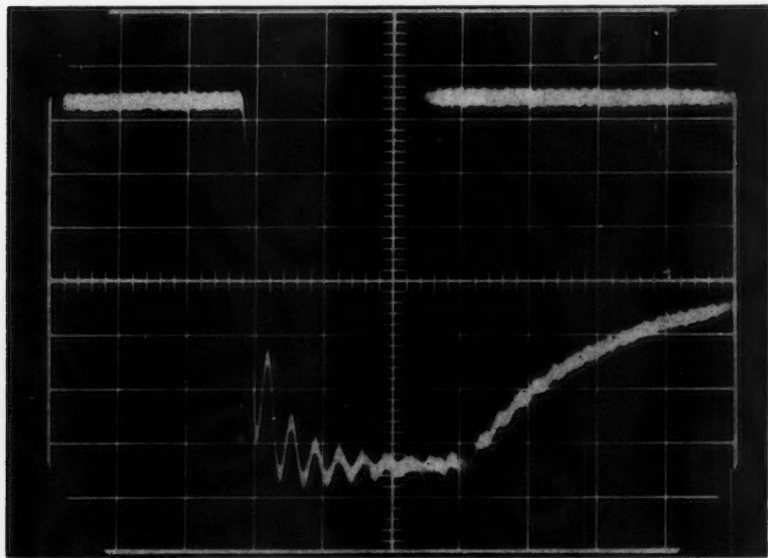


FIG. 4. Temperature oscillation shock-excited by an expansion.

33 cycles/sec. After the cotton batten plug P was stuffed into the lower end of the tube I (see Fig. 1) both the spontaneous and shock-excited temperature oscillations in the gas were damped out and did not reappear in any subsequent run.* All the later expansions were then similar to that shown in Fig. 2.

2.3 Results

At each of seven temperatures, from 1.7 to 4.2° K, from 10 to 25 expansions were performed. In any such run the initial temperature T_1 was kept constant. The cooling ΔT was subsequently measured from enlargements of the photographs of the C.R.O. trace. At any temperature, large expansions produce persistent fogs of helium from the supersaturated vapor, whereas small expansions produce no condensation. Each series of expansions was performed

*We are grateful to Dr. L. C. Jackson for this suggestion.

in such a way as to try to determine the critical supercooling required to produce visible condensation. As this threshold supercooling is more nearly realized, the condensation produced sometimes seemed to be only a few large drops like rain, or else a brief flash of fog. The measurements finally give two numbers for any initial temperature T_i , viz. a maximum temperature drop ΔT_{no} giving no visible condensation, and a minimum temperature drop ΔT_{yes} giving visible condensation. Presumably the true threshold lies between these two numbers. Figure 5 is a graph of these measurements showing ΔT_{no} as circles and ΔT_{yes} as plus signs. At 1.7° K the + point is believed to be rather high because the vapor density is so low (1/50 of its value at 4.2° K) that the first condensation may not have been seen. The accuracy of the other points is probably no better than ± 5 mdeg.

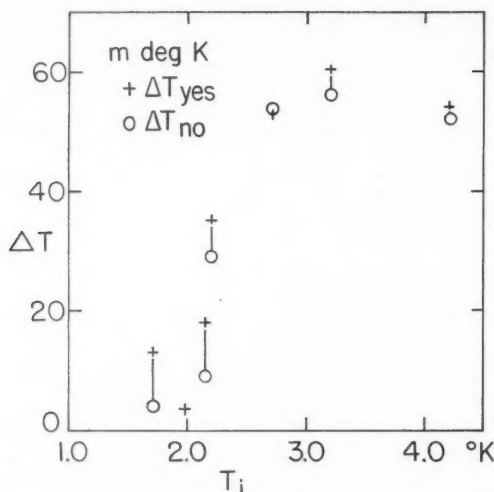


FIG. 5. Maximum temperature drop ΔT_{no} which gives no visible condensation, and minimum temperature drop ΔT_{yes} which gives condensation, as a function of the temperature T_i before expansion of saturated He^4 vapor.

3. ANALYSIS

3.1 Supersaturation of an Imperfect Gas

We follow Wilson (1897) in defining supersaturation, S , as the ratio of the actual density of the vapor ρ_t immediately after expansion to the saturation density ρ_{ts} at the lower final temperature T_t . Only when the vapor is an ideal gas does this definition become equivalent to P/P_∞ where P is the actual pressure and P_∞ is the saturation vapor pressure over a plane surface.

We wish to find a method of calculating S from the measured cooling ΔT , without having to assume that the expanding gas is ideal. The initial conditions before expansion are: $P_i = P_{is}$ the saturated vapor pressure, $V_i = V_{is}$ the saturated molar volume, and T_i . After adiabatic expansion through the critical temperature interval ΔT , we have P_t , V_t , and $T_t = T_i - \Delta T$.

We wish to evaluate the critical supersaturation

$$S \equiv \frac{\rho_t}{\rho_{ts}} = \frac{V_{ts}}{V_t}$$

where V_{ts} is the saturated molar volume at the final temperature. Now

$$V_{ts} = V_{ts} + \int_0^{\Delta T} \left(\frac{dV}{dT} \right)_{\text{SVP}} dT = V_{ts} + \left(\overline{\frac{dV}{dT}} \right)_{\text{SVP}} \Delta T$$

where $\left(\overline{dV/dT} \right)_{\text{SVP}}$ is the average rate of change of molar volume along the saturated vapor curve. And $V_t = V_{ts} + \Delta V_s$ where ΔV_s is the actual change in molar volume during the adiabatic expansion.

We now calculate ΔV_s for an imperfect gas. First we obtain a relationship between V and T in an adiabatic change. The equation of state of any gas may be written as $f(T, V, S) = 0$ where S is now the entropy.

Then

$$\begin{aligned} \left(\frac{\partial T}{\partial V} \right)_S &= - \left(\frac{\partial T}{\partial S} \right)_V \left(\frac{\partial S}{\partial V} \right)_T \\ &= - \frac{T}{C_V} \left(\frac{\partial S}{\partial V} \right)_T \\ &= - \frac{T}{C_V} \left(\frac{\partial P}{\partial T} \right)_V \end{aligned}$$

by one of Maxwell's relations. Now for any imperfect gas the equation of state may be written as a volume virial expansion

$$PV = RT \left(1 + \frac{B}{V} + \frac{C}{V^2} + \dots \right).$$

Then

$$\begin{aligned} T \left(\frac{\partial P}{\partial T} \right)_V &= \frac{RT}{V} \left(1 + \frac{B}{V} + \frac{C}{V^2} + \dots \right) \\ &= P \text{ for an imperfect gas (and for an ideal gas also).} \end{aligned}$$

So

$$\left(\frac{\partial T}{\partial V} \right)_S = - \frac{P}{C_V}.$$

And hence

$$\Delta V_s = - \int_{P_1, T_1}^{P_t, T_t} \frac{C_V}{P} dT = - \left(\overline{\frac{C_V}{P}} \right) \Delta T.$$

Thus the supersaturation

$$(3.1) \quad S = \left[V_{ts} + \left(\overline{\frac{dV}{dT}} \right)_{\text{SVP}} \Delta T \right] \left[V_{ts} - \left(\overline{\frac{C_V}{P}} \right) \Delta T \right]^{-1}.$$

This is the expression desired.

3.2 Temperature Dependence of the Critical Supersaturation

In order to apply eq. (3.1), we need detailed information of the equation of state of the saturated vapor. (C_v/P) values were obtained by graphical averaging of the measurements of van Itterbeek and Laet (1958). The values of V_{ls} and $(dV/dT)_{SVP}$ used were calculated from the refractive index data of Edwards (1957) for He⁴-saturated vapor. The Lorenz-Lorentz law was used, taking as the polarizability of He⁴ vapor, the liquid value (Edwards 1958) of $(0.12454 \pm 0.00021) \text{ cm}^3 \text{ mole}^{-1}$. Thus,

$$(3.2) \quad V_{ls} = (0.521672 \pm 0.00089)(n^2 + 2)(n^2 - 1)^{-1},$$

where n is the refractive index, was used to calculate the saturated molar volumes from Edwards' (1957) data.

Table I shows the resulting critical supersaturations taking the critical supercooling ΔT_c to be the average of the ΔT_{yes} and ΔT_{no} points of Fig. 2. The

TABLE I

Condensation data for He⁴, showing final temperatures, critical supercooling, experimental and theoretical critical supersaturations, and critical radii, and number of molecules per droplet calculated by two different methods

T_f , ° K	ΔT_c , mdeg K	S , expt.	S , theory	r_K , Å	g_K	r_F , Å	g_F
4.181	53.0	1.018	1.077	104	8.84×10^4	61.7	1.84×10^4
3.147	58.2	1.033	1.297	137	2.26×10^5	66.3	2.56×10^4
2.671	53.6	1.047	1.549	135	2.21×10^5	73.5	3.58×10^4
2.167	32.2	1.045	2.129	202	7.58×10^5	118.	1.53×10^5
2.139	13.6	1.020	2.206	465	9.22×10^5	280.	2.03×10^5
1.980	3.8	1.007	2.586	1570	3.52×10^8	950.	7.86×10^7
1.705	8.5	1.022	3.593	579	1.77×10^7	392.	5.49×10^6

results show that down to about 2.2° K a lower temperature requires a greater supersaturation to produce condensation. Below about 2.2° K there seems to be a drop in the critical supersaturation required. Because of the rapidly decreasing vapor density and therefore the added difficulty in observing condensation, the critical supercooling ΔT_c seems more likely to have been overestimated than underestimated at these lowest temperatures. Such an error, if present, would then tend to make the critical supersaturations at the lowest temperatures appear too high, rather than too low.

Volmer and Flood (1934) and later Farley (1952) have discussed the kinetics of the condensation process and have predicted that the temperature variation of the critical supersaturation should be given by

$$(3.3) \quad \frac{P}{P_\infty} = \exp \left[K \left(\frac{\sigma}{T} \right)^{3/2} V_l \right]$$

where K is a constant, empirically equal to 0.557 according to Volmer and Flood. σ is the surface tension of the liquid, T is the absolute temperature, and V_l is the molar volume of the liquid.

P/P_∞ is only 0.7% less than $S (= V_{ls}/V_l)$ at 4.18° K, and still closer at lower temperatures; as may be verified using the second and third virial

coefficients for He⁴ gas. In Table I the values of (P/P_∞) calculated from eq. (3.3) are shown as S (theory). It is clear that the predicted temperature variation of S is far greater than is observed experimentally.

In these calculations we used the data of Allen and Misener (1938) for σ , and obtained V_l from Edwards (1958) data of liquid He⁴ density.

3.3 The Mechanism of Condensation

It has long been recognized that condensation requires nucleation (see, for example, Wilson 1951). Dust particles in water-saturated air are known to be very effective as condensation nuclei. Ions are also known to be effective—this fact leads to the usefulness of cloud chambers in tracking ionizing particles. Even in the absence of foreign particles or ions, however, condensation can take place, by self-nucleation, at what is sometimes referred to as the 'cloud limit'.

The possibility that the condensation in our experiments occurred on foreign nuclei or on ions cannot be entirely ruled out. However, care was taken to avoid vacuum leaks which might produce solid air on the walls of the Inconel tube I (see Fig. 1) which might become dislodged during an expansion and fall into the chamber. The cotton batten plug P and the bakelite spacer A would of course tend to stop any such particles before they could enter the chamber.

No experiments were undertaken to determine the effect of ionization on the condensation thresholds. However, the high energy (46 ev) required to form an ion pair in helium gas at low temperatures (Hanauer *et al.* 1959) and the reasonably high density of the clouds produced in our chamber are taken as evidence that we were studying self-nucleated condensation of ion-free vapor. In this case the condensation nuclei are presumed to be embryonic droplets of neutral molecules arising accidentally from density fluctuations in the vapor. The range of sizes of these embryonic droplets is assumed to be larger for higher supersaturations, until finally some of the embryonic droplets exceed a critical size and then persist. When this size is reached, the vapor is then in unstable equilibrium, since smaller drops will tend to evaporate and larger drops will tend to grow. The critical radius is usually calculated using Kelvin's equation (Thomson 1870)

$$(3.4) \quad r_K = \frac{2\sigma V_l}{RT \ln (P/P_\infty)}$$

where r_K is the critical radius, R is the gas constant per mole, σ is the specific surface energy of the droplet (Frenkel (1946, p. 368) has stated that this is equivalent to the ordinary surface tension corresponding to $r = \infty$), V_l is the liquid molar volume, P is the vapor pressure over a drop of radius r_K , and P_∞ is the saturated vapor pressure over a plane surface ($r = \infty$) at the absolute temperature T . Equation (3.4) has been derived also by Frenkel (1946, p. 368) and Farley (1952).

In its derivation, the density of the vapor is neglected in comparison to the liquid density, and the vapor is treated as an ideal gas. It is hardly likely that the assumption of ideality is justified here, since the condensation process

clearly requires interactions between molecules. Moreover, it should be noted that for substances which condense at small supersaturations, eq. (3.4) suggests very large critical radii, tending to infinity as the supersaturation tends to unity. In order to make some comparison of this theory with our experiments, we show the result in Table I of the critical radii, calculated according to eq. (3.4), but replacing P/P_∞ by our experimental values of the supersaturation S .

Frenkel (1946, p. 373) has also given an expression for the critical droplet radius, which may be written

$$(3.5) \quad r_F = \frac{2\sigma V_1 T}{L\Delta T}$$

where L is the latent heat per mole, and ΔT is the undercooling required to produce condensation. Equation (3.5) is derived from eq. (3.4) with the aid of the Clapeyron-Clausius equation (which does not hold exactly here because the Gibbs's functions are not exactly equal inside and outside of the drop (Pippard 1957)). Table I shows the critical radii, r_F , calculated using eq. (3.5) and our directly measured critical supercoolings, ΔT_c . It will be noted that these values are between 1.5 and 2.1 times smaller than those given by eq. (3.4). The latent heats, L , used were those of Berman and Mate (1958) for the three highest temperatures, and the smoothed values collected by van Dijk and Durieux (1957) for the lower temperatures.

The number of molecules, g , in a droplet of critical radius is also shown, in Table I, for r_K and for r_F . These numbers are very high compared with other substances, e.g., for water, where g is less than 100. (Das Gupta and Ghosh (1946, p. 238) calculated $g = 10^4$ for water, but their calculation involved a numerical slip.)

Farley (1952, p. 538) has calculated the number of drops per cubic centimeter, N^* , in a supersaturated system which may be expected to reach the critical size r_K . He gives

$$(3.6) \quad N^* = N_0 \exp(-4\pi\sigma r_K^{2/3} kT)$$

where N_0 is the number of vapor molecules per cm^3 and k is Boltzmann's constant. From the data of Table I, N^* is equal to 2.5×10^{-326} drops per cm^3 at 4.181°K and 8.4×10^{-1570} drops per cm^3 at 3.147°K . For lower temperatures the values of N^* are even smaller. This implies that no helium droplets as large as r_K could appear statistically.

We therefore conclude that the present state of the theory of homogeneous nucleation is inconsistent with our data. Whether this is a defect of the underlying assumptions, or, as seems more likely, is due to the "ideal gas" and other approximations made in the theoretical treatment, is not at present clear.

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REFERENCES

- ALLEN, J. F. and MISENER, A. D. 1938. Proc. Cambridge Phil. Soc. **34**, 299.
BERMAN, R. and MATE, C. F. 1958. Phil. Mag. **3**, 461.
DAS GUPTA, N. N. and GHOSH, S. K. 1946. Revs. Modern Phys. **18**, 225.
EDWARDS, M. H. 1957. Phys. Rev. **108**, 1243.
——— 1958. Can. J. Phys. **36**, 884.
FARLEY, F. J. M. 1952. Proc. Roy. Soc. (London), A, **212**, 530.
FRENKEL, J. 1946. Kinetic theory of liquids (Clarendon Press, Oxford).
HANAUER, S. H., DABBS, J. W. T., and ROBERTS, L. D. 1959. Bull. Am. Phys. Soc. Ser. II, **4**, 6.
KEESOM, W. H. 1942. Helium (Elsevier Pub. Co., Inc., Amsterdam), p. 174.
KRAMERS, H. A. 1949. Physica, **15**, 971.
PIPPARD, A. B. 1957. Elements of classical thermodynamics (Cambridge University Press, London), p. 110.
STACHÓRSKA, D. 1954. Ann. Univ. Mariae Curie-Skłodowska, Lublin-Polonia, **7**, 117.
——— 1956. Acta Physica Polon. **15**, 5.
TACONIS, K. W., BEENAKKER, J. J. M., NIER, A. O. C., and ALDRICH, L. T. 1949. Physica, **15**, 733.
TER HAAR, D. 1955. Proc. Conf. de Physique des Basses Températures, Paris, p. 347.
THOMSON, W. (later Lord Kelvin). 1870. Proc. Roy. Soc. Edinburgh, **7**, 63.
VAN DIJK, H. and DURIEUX, M. 1957. Progress in low temperature physics, edited by C. J. Gorter (North Holland Publ. Co., Amsterdam), p. 431.
VAN ITTERBEEK, A. and DE LAET, W. 1958. Physica, **24**, 59.
VOLMER, M. and FLOOD, H. 1934. Z. Phys. Chem. **170**, 273.
WILSON, C. T. R. 1897. Proc. Roy. Soc. (London), **61**, 240.
WILSON, J. G. 1951. The principles of cloud chamber technique (Cambridge University Press, London), p. 1.

A CONDENSER MEMORY UNIT FOR IMPROVING SIGNAL-TO-NOISE RATIOS¹

D. M. HUNTEN

ABSTRACT

The unit contains 30 low-leakage condensers which can store a signal for several hours if necessary. If the signal is repeated over and over, the successive scans can be added in and the signal-to-noise ratio builds up as the square root of the number of repetitions. In principle, the final signal-to-noise ratio is only slightly better than would be obtained from a single scan stretched out to fill the same total time, but in practice the result may be considerably better, especially if the signal fluctuates slowly. It has been used successfully in several investigations of twilight spectra with photoelectric and photoconductive spectrometers. The original version took 1 minute per scan and was rather bulky; a recent modification can scan 32 channels in 10 seconds if required.

1. INTRODUCTION

A problem which arises in many lines of research is the measurement of repetitive signals in the presence of noise. We have in mind especially the photoelectric spectra of aurora and twilight, or similar faint and somewhat variable sources, and will discuss the matter with reference to this particular case; thus, one repetition will be called a scan. If the signal-to-noise (S/N) ratio is inadequate it can be improved by increasing the time of observation, and this is normally done by slowing down the rate of scan and increasing the time constant of the filter. But if the source is an aurora, the total intensity may vary so much during the scan that the results are useless, even if the length is only 1 minute; and this time is often insufficient. Although twilight does not vary nearly so quickly, great difficulty would still be present in interpreting a 10-minute scan. The other possibility is to take a large number of short scans and average them, or what is essentially the same thing, add them together. This has sometimes been done manually from a number of recorder tracings, but an automatic method is obviously much to be preferred. It is not difficult to show that for a constant source this scheme gives the same S/N ratio as a single scan taking the same time, but for a fluctuating source the averaging method is far superior. In addition, the method to be described lends itself naturally to time integration of the signal in each channel, and thus provides a further small factor of improvement over the conventional one. Any device which can add successive scans must be able to store information and recall it when needed; it is convenient to call it a "memory" and our device will therefore be called a "condenser memory", since the information is stored in the form of voltages on a bank of low-leakage condensers. The stored spectrum is divided into a number of channels, one for each condenser; the bank is scanned in synchronism with the scan of the spectrometer. A

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suitable device adds the new spectrum to the old sum and stores the new sum back in the memory. This adder is the principal novelty of the instrument to be described. The natural field of application of this memory is to scans of several seconds or longer, and to a fairly small number of channels of which 30 is typical.

It is of interest to consider some previous methods which have been used for a similar purpose; the survey does not pretend to be complete, however. A photographic time exposure to the repeating trace on an oscilloscope is described by Bloch and Garber (1949); they were observing nuclear induction signals, but the same technique is fairly common with radar displays. While simple, the method is inefficient because the individual signals are always added even when they should, part of the time, be subtracted. Suryan (1950) used a magnetic recording on a drum rotating in synchronism with the signal; the recording head was moved slowly parallel to the axis so that the signals were impressed along a helical track. The reading head covered the whole drum and added all the signals together. The biggest difficulty with this scheme is its mechanical complexity; but it is not suitable in any case for signals which repeat as slowly as ours, since the drum would rotate so slowly that pickup from it would be too small. Harrington and Rogers (1950) stored radar signals in a storage cathode-ray tube; in a sense, this memory is of the condenser type, but the condensers are so small that the signals leak off in a few seconds at the most; also, the fidelity is not high. A dielectric recording drum described by Anderson (1957) is much better in both respects but was not available when our apparatus was being developed.

A direct ancestor of our system is the memory commutator of Beard and Skomal (1953). Though it rotated much faster, the important difference is that they fed the condensers through a relatively small resistor and allowed each condenser to charge exponentially. Thus if the input signal is constant, the voltage on the condenser will approach it asymptotically. In our system, the voltage continues to rise until the circuit overloads, and can be many times larger than the input; the stored voltage is the true time integral of the input. The device of Beard and Skomal gives the same approximation to this integral that an RC circuit does. The "analogue memory" of Kozak (1958) is rather similar, though used for an entirely different purpose.

The principle of our method is the following. As each condenser is switched into the circuit, the voltage on it is duplicated on a second "transfer" condenser by a special amplifier of unit gain. Then the transfer condenser is switched in series with the incoming signal and the sum voltage duplicated on the memory condenser by the same amplifier. The action is accurate enough so that a stored signal can be read off and back on again a large number of times with little degradation. The condensers used have polystyrene dielectric so that the "absorption" effect is small and a signal can be stored for hours without leaking away. The unit has been found valuable in making accurate measurements on twilight spectra, adding from 10 to 30 one-minute scans for a total "exposure" of as much as $\frac{1}{2}$ hour. Application to aurora has been prevented by the scanning mechanism which could not be

made to go around in 10 seconds; 1-minute scans are too long to be useful with aurora. The new switching scheme described below removes this limitation.

2. OPERATION AND CIRCUITS

The most natural way to add a series of voltages on a condenser is to feed them in succession through a constant-current device, such as a large resistor or a suitable type of feedback amplifier. But for a bank of condensers this has the serious disadvantage that the voltage generated is inversely proportional to the capacitance, so that all the condensers must be closely matched. The method to be described operates on voltages instead of currents and is therefore independent of capacitance. Moreover, it gives a readout of the stored signal which may be observed during operation. It is based on a precision voltage follower shown as the triangle in Fig. 1. This device accepts a signal at a very high-impedance level, drawing essentially no current, and reproduces it at a low impedance with negligible error, estimated to be less than 0.01%.

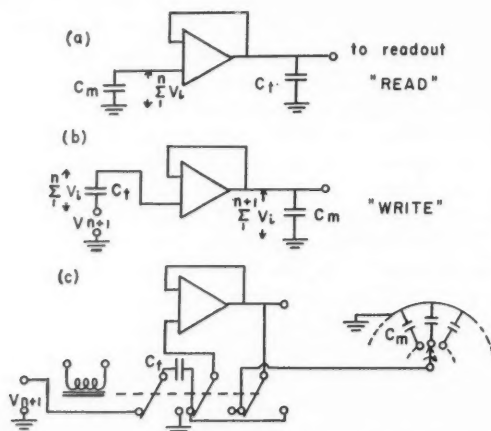


FIG. 1. (a) Effective circuit of the memory while reading from one condenser in the bank. The triangle represents a voltage follower with a gain very close to 1.

(b) Circuit for adding the input and storing the result back in the bank.

(c) Actual circuit shown with the relay in the (b) position.

First let the follower be connected as in Fig. 1(a). C_M represents one of the condensers in the memory bank and C_T is a "transfer" condenser. Whatever voltage is on C_M will be reproduced on C_T and is also available for monitoring. If the circuit is then switched into the arrangement of Fig. 1(b) the voltage on C_T is connected in series with the input from the spectrometer, and the sum will appear on C_M . The next time this action is repeated, a new C_M is in the circuit. The switching is done by the three-pole relay shown in Fig. 1(c) which is drawn in the (b) position. The input voltage does not come directly from the spectrometer, but passes first into a feedback integrator (Korn and

Korn 1952) which is reset to zero just after the end of part (b) of the memory cycle. Thus, the voltage in each condenser of the bank is the integral of the signal for the total time it has been in the circuit.

The follower itself is essentially a high-gain direct-coupled amplifier with 100% negative feedback. The circuit is shown in Fig. 2; it was developed after a brief qualitative description by Bousquet (1956). It can be regarded as a three-stage cathode follower; the output is fed back to the first tube by the

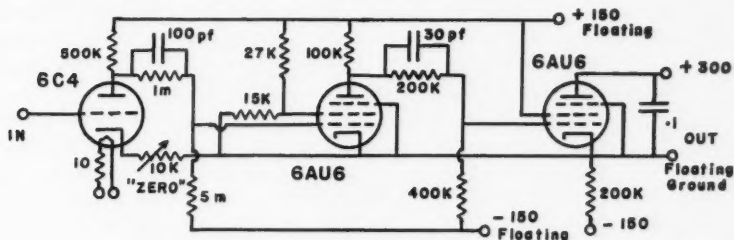


FIG. 2. Circuit of the follower.

common cathode connection. For some purposes it is also useful to regard the circuit in the following way: transfer the ground from the end of the source to the common cathode connection, leaving the source floating between the input and the plate of the third tube. The essentials of this arrangement are shown in Fig. 3. The 220-k Ω resistor now acts as the plate load of the third stage, even though it is on the other side of its power supply. The amplifier

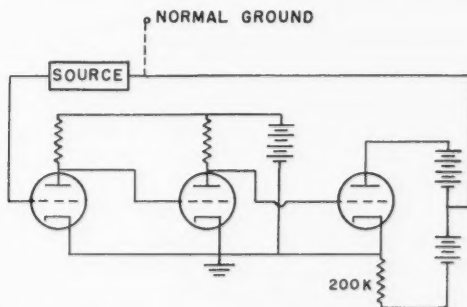


FIG. 3. The circuit of Fig. 2 with a different ground point.

is thus an ordinary three-stage one except that 100% feedback is applied through the floating source. The loop gain will be about 10^5 for the circuit shown; thus the external gain should be 0.99999. This large loop gain means that there is great danger of high-frequency oscillation; the condensers in the plate circuits control the shape of the high-frequency cutoff to prevent this.

The high loop gain is realized only if the plate and bias power supplies can float along with the output as indicated in Fig. 2. We have used a single 350-volt supply feeding two miniature regulator tubes; the complete circuit thus includes five tubes and a rectifier. Normal grounded supplies provide the plate and cathode-return voltages of the last stage; they need not be regulated. The rheostat at the cathode of the 6C4 allows the level of the output to be set equal to that of the input; this must be done rather accurately or the voltages stored in the memory will drift by twice the offset each time the information is cycled. Often a small drift of this sort is not important, since all channels are affected the same, but a large drift might take the circuit out of its range of correct operation. The first stage operates with low heater and plate voltages so that the grid current is less than 10^{-10} ampere.

If the output of the follower is connected to a condenser at a considerably different potential, it may not be able to supply the required current and the output will not be able to follow the input for a moment. During this moment the input may draw a large burst of current. To eliminate this trouble, the series resistors shown in Fig. 1(c) are included; they must be small enough to let the condensers charge fully during the time available. More charging current could be made available by replacing the third tube with a power tetrode; this would be useful in a memory with a very short time per channel.

3. SWITCHING

The very low leakage of a polystyrene condenser is realized only if there are no leakage paths in parallel with it. This dictated the design of the commutator in the first version, since no ordinary switches of adequate performance were available. The condensers were arranged in a circle and contact springs attached to and supported by the inside terminal of each; the arrangement was similar to the sketch in Fig. 1(c). An arm carrying another contact was rotated in steps to make connection to each in turn. The intermittent motion was obtained from a synchronous motor driving through a six-point Geneva movement and then a 1:5 gear ratio. This operated well at a rate of one step in 2 seconds, but would not quite keep time at three steps per second. Probably a slightly more powerful motor would have been able to run at the fast speed, but this was not pursued.

The shaft which drove the Geneva movement also carried a cam which operated a microswitch and thereby the relay shown in Fig. 1(c). It was left in the "read" position while the commutator was switching, and for a short time after, so that the transfer condenser could become fully charged; the "write" part of the cycle occupied the rest of the time, a little less than half. Just after the end of the "write" operation, the integrator at the input was reset to zero by another relay making a brief contact. At first this was operated by a second cam, but later by a transient generated when the transfer relay moved to the "read" position. Not only is this simpler; it also guarantees synchronization between the two relays.

A much more compact and faster arrangement is possible by taking advantage of the properties of the "Glaswitch", or dry-reed switch, as suggested by

Helmer and Hemmendinger (1957). This switch has the high insulation resistance needed, and the commutator may be an ordinary one occupying little space. The high speed of the Glaswitches suggests their use also for resetting the integrator. The commutator available required the use of 32 channels instead of 30.

It is worth while to pay some attention to the method of setting all the condensers to zero initially. The easiest to build is a switch to ground the wiper of the commutator, or the equivalent point if the Glaswitches are used. But it is often inconvenient to have to wait for a complete cycle of the memory, and a separate shorting bar which can connect to all the condensers at once is preferable.

A switch should be provided to lock the transfer relay in the "read" position. Then the contents of the memory remain undisturbed and may if desired be observed one or more times. This switch can also be used to start the memory operating at any suitable time after it has been set to zero.

4. OPERATION

The contents of the memory are easily recorded on a strip-chart potentiometer; the output of the follower is a low-impedance point and can drive a calibrated voltage divider or a helical potentiometer so as to give a suitably low voltage. The recording in memory should be made at as high a voltage level as possible to reduce the importance of drift and other stray voltages; the output may then be attenuated to the magnitude required by the recorder. It is often useful to follow the accumulation of the signal on the recorder; if any large interfering pulses are stored, they can be allowed for. Records of this sort show two steps per channel, corresponding to the old and new contents. A record made at the end of the run with the transfer relay off shows only one. The final recording may be repeated several times if desired until the best settings of gain and time constants are found.

An example of a run on the sodium *D* lines in the twilight is shown in Fig. 4 (Lytle 1958). The way in which the S/N ratio builds up as more and more spectra are included may be observed. The lines appear above a continuum caused by nonresonant scattering in the atmosphere. The width of the lines and their triangular shape arise entirely from the spectrometer; there is no detectable degradation introduced by the memory except for the steps corresponding to the individual channels. The area of a line recorded in this way is a good measure of its intensity; it is easily found by adding up all the steps within the line. The fact that the intensity ratio of the two lines is much less than the normal 2:1 results from self-absorption in the sodium layer in the upper atmosphere (Chamberlain, Hunten, and Mack 1958). The measurements could not have been made with nearly as much accuracy without the memory; a single 12-minute scan would have been hopelessly distorted by variations in intensity and atmospheric transparency.

The memory was also used by Harrison to study the O₂ band discovered by him in the twilight at 1.58 microns (Vallance Jones and Harrison 1958). He was able to use much better resolution than would otherwise have been

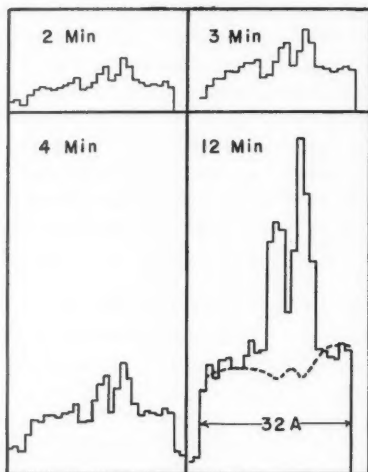


FIG. 4. Part of a run on the *D* lines in twilight.

possible. The intensity decays with a half-life of about 30 minutes, so that single long scans are again not practical. But 30 scans of 1 minute each added up by the memory gave a useful result and allowed the band to be identified.

A search for the potassium resonance line at 7699 \AA in twilight has recently been carried out by Lytle (1958). In this case the radiation was not detected, but use of the memory enabled the limit of detection to be set much lower than would otherwise have been possible. It appears that other studies of twilight may also be made possible by this new technique, which offers a considerable increase in available sensitivity and permits photoelectric spectrometers to compete on nearly equal terms with fast spectrographs. It is expected to be just as valuable for studies of the auroral spectrum now that it can be used with a 10-second scan. Until now, only the brighter auroral forms gave a large enough signal for quantitative studies; the fainter forms are not only much more plentiful, but may also give different results.

Many studies would profit from the use of a memory with more channels than the 30 to 32 used here; and a faster repetition rate might also be useful. It is doubtful if the present adding unit would operate well beyond three or four channels per second; and it might be economic to make a condenser memory with 64 channels or even 96. It is likely that the capacitance of the condensers could be reduced to 0.1 microfarad without impairing the operation; but there is no point in reducing their cost much below the cost of the switching system. With this in mind, the best size is probably about 0.2 microfarad.

A great increase in both speed and number of channels is possible by adopting digital-computer techniques, as has been done widely in recent years for multichannel pulse-height analyzers (Hutchinson and Scarrott 1951; Schultz, Pieper, and Rosler 1956). The memory requirements for the two

purposes are almost identical, except that fast random access to any channel is important in most cases in nuclear physics, but is of no importance whatever here. The ultrasonic delay-line memory is then just as good as the more expensive magnetic-core type. It has also the advantages that the stored spectrum is continuously displayed on a cathode-ray tube, and that information may be read in and out at arbitrary rates, simultaneously if desired.

If a speed of five channels per second is sufficient, another possibility is to record the individual spectra in digital form on punched paper tape, similar to teletype tape. This may later be read into a general-purpose digital computer and the averaging done by a suitable program. This requires much less equipment, as long as the computer is available, but has the disadvantages that the averaged spectrum is not immediately visible; if anything has gone wrong, it will not be known until the next day. If the observations are of an experiment that can be repeated, this is of little importance; but it may be very important for observations of uncontrolled natural phenomena.

It is a pleasure to acknowledge the help of several colleagues with the construction and testing of the instrument: A. W. Harrison, G. F. Lyon, E. A. Lytle, and J. F. Noxon.

REFERENCES

- ANDERSON, V. C. 1957. *Rev. Sci. Instr.* **28**, 504.
BEARD, C. I. and SKOMAL, E. N. 1953. *Rev. Sci. Instr.* **24**, 276.
BLOCH, F. and GARBER, D. H. 1949. *Phys. Rev.* **76**, 585.
BOUSQUET, A. G. 1956. *General Radio Exp.* **30** (10).
CHAMBERLAIN, J. W., HUNTEN, D. M., and MACK, J. E. 1958. *J. Atmospheric and Terrest. Phys.* **12**, 153.
HARRINGTON, J. V. and ROGERS, T. F. 1950. *Proc. I.R.E.* **38**, 1197.
HELMER, R. J. and HEMMENDINGER, A. 1957. *Rev. Sci. Instr.* **28**, 649.
HUTCHINSON, G. W. and SCARROTT, G. C. 1951. *Phil. Mag.* **42**, 792.
KORN, G. A. and KORN, T. M. 1952. *Electronic analog computers* (McGraw-Hill Book Co., Inc.).
KOZAK, W. S. 1958. *Can. Electronics. Eng.* **2** (2), 38.
LYTLE, E. A. 1958. M.Sc. Thesis, University of Saskatchewan, Saskatoon, Saskatchewan.
SCHULTZ, H. L., PIEPER, G. F., and ROSLER, L. 1956. *Rev. Sci. Instr.* **27**, 437.
SURYAN, G. 1950. *Phys. Rev.* **80**, 119.
VALLANCE JONES, A. and HARRISON, A. W. 1958. *J. Atmospheric and Terrest. Phys.* **13**, 45.

IMPURITY CONCENTRATION PROFILES IN ICE BY AN ANTHRONE METHOD¹

M. SMITH AND E. R. POUNDER

ABSTRACT

Solutions of sodium carboxymethyl cellulose (CMC), sodium chloride, ethylene glycol, and ethyl alcohol in water were prepared and frozen under controlled conditions. The ice in each case was divided into horizontal sections, melted, and the amount of each impurity measured. The organic liquid and salt concentrations were found from refractive index values using a dipping refractometer, and the CMC content, after treatment with an anthrone solution, was measured with a spectrophotometer. Developments in the anthrone method are described. Qualitative tests were also made by freezing solutions of soluble dyes.

In the freezing of aqueous solutions of CMC and the dyes, rejection of the impurity is almost complete. When solutions of salt or alcohol or glycol in water, or of CMC and alcohol or glycol in water, are frozen a surface concentration peak and a second peak about 7 mm below the surface, corresponding to a previously observed discontinuity in the crystal structure of impure ice, are found. The ability of alcohol or glycol to carry CMC or a dye to places in the ice structure not available to them in the absence of the organic liquid is noted.

INTRODUCTION

It has been shown by Perey and Pounder (1958) that when water containing added foreign material is frozen, a transition layer indicating a radical change in crystal structure is clearly visible at a distance of the order of 1 cm below the surface. It was assumed that such change is associated with changes in concentration of the added foreign material. The present work was undertaken to verify the assumption by quantitative measurement of the distribution of the foreign material in the ice.

It seems probable that impurity distribution is a major factor in determining the mechanical properties of any form of impure ice (see Pounder 1958). This is particularly true in the extremely important case of sea ice.

According to a theory suggested by Anderson (1958) and elaborated by Assur (1958) the properties of sea ice are very largely dependent on the distribution of salts and brine within the ice. In the present work additive materials other than those found in sea water have been studied but one example is included where pure sodium chloride was the additive and it is hoped to extend the work in this direction soon.

METHODS OF MEASUREMENT

The impure melts studied by Perey and Pounder (1958) contained various alcohols and other organic solvents, and a variety of carbohydrates, particularly sodium carboxymethyl cellulose (grade D435 as supplied by Chemical

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Contribution from the Ice Research Project, Department of Physics, McGill University, Montreal, Que.

Developments of Canada, said to contain a minimum of 66% sodium carboxymethyl cellulose, the other salts present being principally sodium chloride and sodium glycolate).

It was decided to confine the present quantitative analyses largely to D435, ethyl alcohol (Reliance Chemicals 650P = 82½% by volume), and ethylene glycol (Purified Fisher Laboratory Chemical). Since the behavior on freezing of CMC and sodium chloride is quite different as far as rejection is concerned, it is unfortunate that grade D435 contains some sodium chloride. No grade of CMC free of sodium chloride was available, however, and in any event the concentrations of D435 used in freezing tests were so low (about 0.15% by weight) that the small amount of sodium chloride contained in it introduced negligible errors in the tests for CMC and alcohol or glycol. All of the tests were made with D435 samples from a single batch so that the composition of the D435 was assumed to be uniform.

Ethylene glycol was chosen to provide, with the alcohol, examples of both relatively non-volatile and volatile solvents; they serve also as examples of both heavier than water and lighter than water solvents.

The method which was found to be the most suitable for D435 estimation was a spectrophotometric technique which will be referred to as the anthrone method. This method consists essentially of adding anthrone in solution to the test samples. When a carbohydrate (CMC in these tests) is present, a green color develops through chemical reaction between the anthrone and the carbohydrate. The optical density of the solution, as measured with the spectrophotometer, can be used to calculate the concentration of CMC and hence of D435 in the test sample. It was found convenient to use the concentration of D435 in calibrating the method as well as in citing results.

The anthrone method was suggested by Dreywood (1946) of the Eastman Kodak Laboratories as a qualitative general test for carbohydrates. It has been carefully developed for quantitative use by Black (1951) at the DuPont Laboratories and is frequently quoted in research literature.

Its use, however, presents several difficulties; the results vary for example with the temperature at which the reaction takes place, with the age of the reagent and of the solution, with the acid concentration, and with the degree of substitution of the sodium carboxymethyl cellulose. The presence of various other carbohydrates or their derivatives interferes with the reaction. Black states that calibration curves should be made every 2 or 3 weeks and that the reagent used should be between 4 and 24 hours old. Under these conditions Black achieved a relative accuracy of 2%, if the degree of substitution was known. The anthrone is dissolved in sulphuric acid and the quantities used are large (50 ml of 60% acid for each test), so that in 1 day of testing it might be necessary to use, and dispose of, about 1500 ml of 60% sulphuric acid.

A modification of the method has been suggested by Loewus (1952). Loewus used ethyl acetate as solvent for the anthrone and states that this prevents the gradual darkening of the reagent which occurs when the solvent is sulphuric acid, a darkening which varies with any slight changes in the purity of the sulphuric acid. The expected accuracy is not stated in his paper.

As used in tests in this laboratory Loewus' modification was very disappointing in accuracy, in consistency, and with regard to the aging of the reagent. Further the results were affected by the alcoholic content of the samples tested, making its use impossible for this investigation.

In two recent papers, Scott and Melvin (1953) and Mokrasch (1954) returned to dissolving anthrone in sulphuric acid but stored it in a cool dark place and emphasized the importance of controlling the temperature of samples and reagent before mixing. Scott and Melvin used 90° C for the development of color; Mokrasch used 80° C.

Scott and Melvin gave a detailed account of sources of errors and felt that standardization is necessary for each set of samples. As they could not compare one day's absorbance with another as an indication of precision, they measured the standard deviation of 97 sets of duplicate blanks and 345 sets of duplicate sample determinations as 0.48% of absorbance at 0.600 absorbance. They found their most important source of error was variation of readings obtained in blank tests. Mokrasch found his reagent to be stable for 2 months when stored at 4° in the dark. He gave no estimate of accuracy.

Roe (1955) has suggested adding thiourea to the reagent as a means of increasing its stability and found that in this way it could be used for 2 weeks when stored in a refrigerator. He states that when the heat of mixing is used as a means of developing color, the accuracy to be expected is only $\pm 5\%$. In Roe's (1954) careful experiments with dextran the coefficient of variation, using duplicates, was $\pm 0.36\%$.

The following procedure has been found most satisfactory in this laboratory and was used in the experiments reported.

Preparation of the Reagent

A 200-ml volume of concentrated sulphuric acid (Fisher Reagent 95-98%) is diluted with 60 ml of distilled water. Both volumes are measured into beakers at room temperature, and the beakers are then cooled in crushed ice before mixing and again after mixing. With the beaker of diluted acid remaining in the ice, 0.200 g of anthrone (Fisher Reagent grade) and 2.000 g of thiourea (Fisher Certified Reagent) are added and stirred until the solution is clear and dissolving seems complete, which takes about half an hour. The resulting reagent is stored in the dark at from 1° to 5° C and, in general, is used within 1 week of preparation.

Test Procedure

Samples of 1 ml each of the solutions to be tested for carbohydrate content are pipetted into screw-top pyrex test tubes. A quantity of 6 ml of the reagent is measured into each of several additional test tubes, using a burette. All test tubes are then cooled for 15 minutes in crushed ice, after which the test solution and reagent samples are mixed in pairs (by pouring backwards and forwards twice) and returned to the crushed ice. The test tubes, with their tops on loosely, are arranged in a rack and plunged into boiling water for 10 minutes, returned to the ice bath again for 5 minutes, and then allowed to stand (covered to exclude light) at room temperature for 20 minutes. After this time, the absorbance of each sample is measured at 620 m μ using a Beck-

man Model B spectrophotometer. This procedure, developed after many trials, insures a precisely controlled and reproducible temperature regime for the color-producing reaction, and gives quite reproducible results for the carbohydrate content.

In each experiment one blank is included by using distilled water instead of a test solution. The optical density of the blank, compared with the reading given by distilled water (without any reagent), serves as a check on the experimental conditions and on the condition of the reagent. A great improvement in consistency is obtained by using the optical density of the blank as zero, rather than that of pure distilled water.

The use of thiourea as one of the components of the reagent not only increases the length of time for which the reagent can be kept without deterioration, but also decreases the variation between successive tests of the same solution.

The measured optical density for D435 solutions was not affected by the presence of ethyl alcohol in the concentrations tested, up to 5% of alcohol.

The method is very sensitive. Up to a concentration of about 200 $\mu\text{g}/\text{ml}$ it is possible to distinguish differences in optical density corresponding to differences in concentration of 1 $\mu\text{g}/\text{ml}$, i.e. one part in a million, but the reproducibility is not as high. There are the uncertainties introduced by the measurement of the volumes of test samples and reagent and by slight variation in the heat treatment, etc. Several authors mention the erratic behavior of reagent aging, and of color stability, and of unaccountable variation in blanks. For single tests the possible error is estimated by us as 2%.

The calibration curve is given in Fig. 1. All D435 solutions were filtered through Whatman's No. 1 filter paper, as this was found necessary to obtain reproducible results, probably because D435 does not form a completely clear aqueous solution. However, the concentration figures plotted on the graph are the original values before filtration. The curve was checked over a period of 5 months, using a number of preparations both of reagent and of standardizing D435 solutions. Each value plotted is thus the average of 6 to 10 measurements. The deviation of individual readings from average values was from 1 to 1.5%.

Tests were made with four different commercial grades of sodium carboxymethyl cellulose (D235, D435, L245, T253 made by Chemical Developments of Canada), in various concentrations and using solutions both filtered and unfiltered.

Using filtered solutions, and plotting optical density against the actual amount of sodium carboxymethyl cellulose in each preparation, according to the manufacturer's specifications, it was found that the values for all four preparations lay along one straight line. This shows that the anthrone test for sodium carboxymethyl cellulose is not affected by the presence of varying amounts of other salts such as are found in these preparations.

Figure 2 illustrates the effect of filtering, using D435. Points marked by crosses were obtained using unfiltered solutions; points marked by circles represent filtered solutions. The concentration values plotted are the values before filtering, in each case.

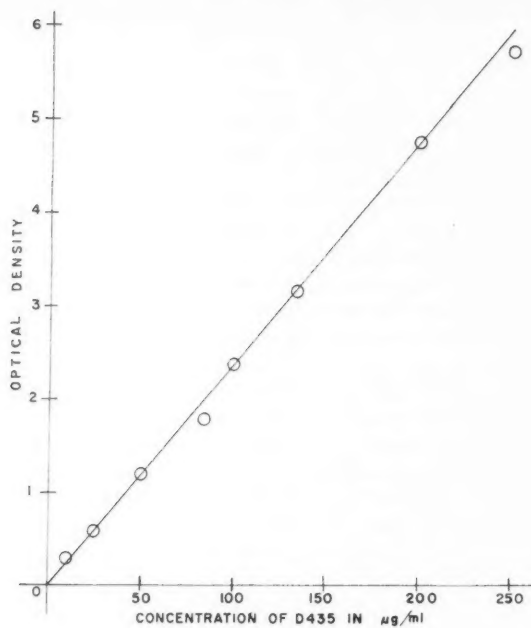


FIG. 1.

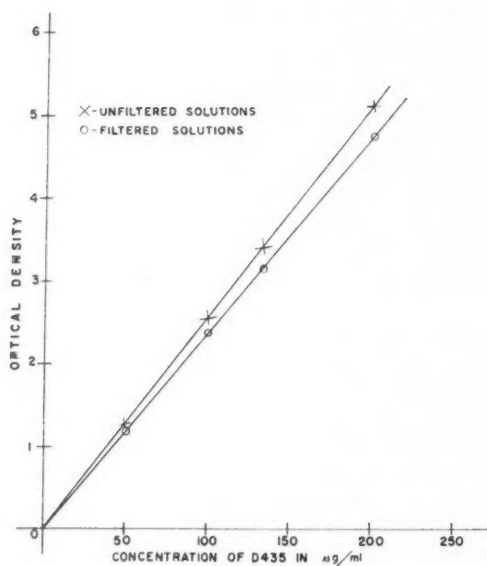


FIG. 2.

At the beginning of this investigation alcohol concentrations were measured by means of distillation and specific gravity measurements, a method both lengthy and uncertain. For most of the work here reported a Bausch and Lomb dipping refractometer was used (with prism A of range 1.32–1.36 refractive index, and occasionally No. 3 auxiliary prism). In it, rays of light (from an incandescent lamp) pass through a beaker containing the sample, and enter the prism. The position of the grazing or critical ray forming the boundary between the light and dark parts of the field of view may be measured.

A calibration curve for alcohol concentration was prepared using solutions containing both D435 and ethyl alcohol in the proportions used in ice preparation, since the D435, or probably the small amount of sodium chloride in it, does raise the values a trifle over those found when using the alcohol alone. This effect is very slight, being undetectable for D435 concentrations of less than 75 μg per ml.

Using a water bath and measuring temperatures to 1/10 Centigrade degree when equilibrium was established, measurements could be made to 1/100 of a scale division. By using an average of 10 determinations these were usually reproducible to ± 0.01 of a scale division. When the auxiliary prism was used (in cases when only small amounts of liquid were available) the uncertainty became at least ± 0.02 of a scale division. Similar calibration curves were prepared for aqueous solutions of ethylene glycol and of sodium chloride, as it was found that the refractive index of these solutions changed appreciably with concentration. This method is much more sensitive, more reliable, and far quicker than the specific gravity method which had previously been used for sodium chloride determinations. A variation of ± 0.02 refractometer scale divisions corresponds, at 25° C, to $\pm 0.016\%$ ethyl alcohol, $\pm 0.008\%$ ethylene glycol, $\pm 0.004\%$ sodium chloride. In these three cases the refractive index varies linearly with concentration in the ranges tested. All concentrations were converted to a standard temperature of 25° C.

PREPARATION OF ICE

For each ice study 1.000 g of D435 was dissolved in 975 ml of distilled water. This was filtered through Whatman's No. 1 filter paper and the volume made up to 975 ml. To this was added 25 ml ethyl alcohol and 5100 ml distilled water, or 25 ml ethylene glycol and 5100 ml water, or 5125 ml distilled water.

About 100 ml was retained for testing, and the other 6 liters of solution were placed in a rectangular plastic vessel about 10 cm deep, surrounded by sufficient insulating material to ensure essentially one-dimensional cooling.

The solution was frozen at a constant ambient temperature, usually -28°C , until solid. The ice was then taken to a cold room kept at -15°C and the sides of the ice block were trimmed off with a band saw, to eliminate edge effects.

In some cases the ice was then divided into horizontal sections with the band saw, the sections were placed in screw-top bottles and then melted at room temperature and analyzed. The minimum thickness of sections obtainable with the band saw is 3 mm (the usual section cut in this way was 9 mm)

and about 1.5 mm of ice is lost between sections in the saw cuts. If the ice is soft the uncertainties of thickness increase.

Where the concentration of impurities in the ice changed rapidly with depth, thinner sections were prepared by either planing the surface of the ice or by melting. Planing is a very tedious, slow process, but very fine sections may be obtained in this way. For melting, the block of ice was held vertically on a horizontal pyrex tray which was gently warmed from below, the melt being poured off in small batches. The thickness of the layers so melted was determined from a knowledge of the dimensions of the block and the weights of the samples. Great care is needed to keep the block vertical as melting proceeds.

The advantages of melting and planing are that they enable very thin layers to be separated, and that no material is lost between sections as it is with saw cuts. It might be expected that the volatile ethyl alcohol would be partially lost by these methods, but the values obtained were consistent with samples prepared by sawing.

RESULTS

Concentration profiles are given for four blocks of ice containing water, D435, and ethyl alcohol; for two blocks of ice containing distilled water and D435 only; and for one block containing pure sodium chloride and water. In all these cases the blocks were frozen at an ambient temperature of -28°C .

In addition profiles are shown for three blocks of ice containing D435 and ethylene glycol, which were frozen at ambient temperatures of -28°C , -19°C , and -5°C respectively.

Some samples of alcohol and water and of glycol and water were frozen in insulated vessels (cylinders about 8 cm in diameter and 7.5 cm deep) and the additive (alcohol or glycol) concentration in the ice measured as freezing proceeded.

As a visual indication of distribution, water-soluble dyes (methylene blue, methyl violet, and eosin) were dissolved in pure water and in water containing a trace of ethyl alcohol, and the solutions frozen.

The concentration profiles for ices I, II, III, and IV, each containing D435 and ethyl alcohol, are shown in Fig. 3, where crosses indicate that the samples were prepared by planing, circles by sawing, and squares by melting. The results for ice I and ice II which were made up from the same stock solution have been combined. This was done because the alcohol values were few and unreliable, some of them having been measured by distillation and specific gravity measurements before the dipping refractometer was available.

It will be seen that there is no inconsistency between values for samples prepared by the different methods. Values for ice I and ice II fit well into the same curve.

The graphs show that the profiles are similar for both D435 and alcohol. At approximately the position of the visually observed transition layer there is a marked peak in the concentration of both D435 and alcohol. It will also be seen that there is a high concentration of both added substances in the

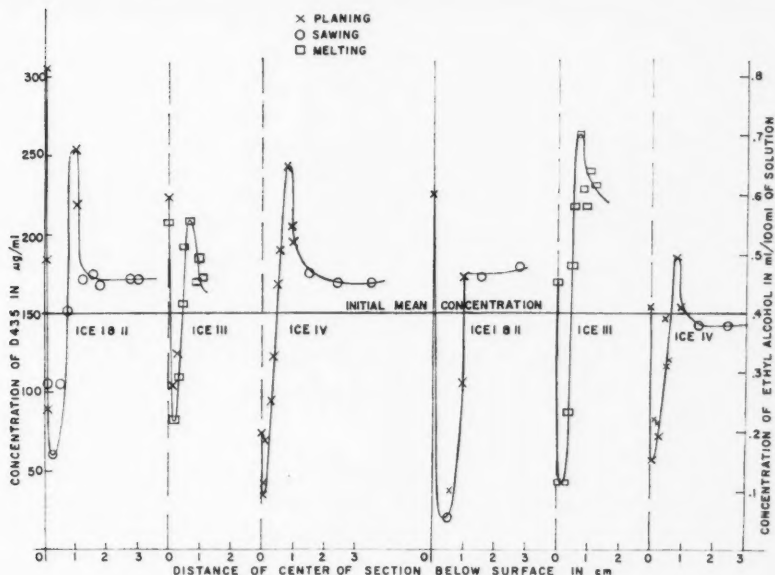


FIG. 3.

surface layer. There is considerable variation in the values obtained at the surface and this appears to result from variations in the thickness of the surface layer examined. It seems probable that the high concentration is confined to a very thin layer, perhaps even a monomolecular layer, and that the concentration drops sharply below this.

Below the transition layer the concentration decreases rapidly to a value which remains fairly constant throughout most of the depth of the block.

To ensure that the variation of the concentration with depths is a consequence only of the freezing process, solutions containing D435 and ethyl alcohol, and D435 and ethylene glycol, both of the same dilution as used in the freezing tests, were left undisturbed at room temperature for some time. The vessels were covered and insulated to guard against evaporation and sudden changes in temperature. After periods of up to 2 weeks, samples carefully pipetted from various levels showed no surface concentration nor any variation in concentration with depth.

Two tests (V and VI) were made with ice containing D435 alone. The results were almost identical and are illustrated for ice V in Fig. 4. A slight concentration was observed in the surface layer but below this the D435 was almost totally rejected from the ice until near the bottom of the vessel where the concentration rose rapidly. Visual inspection foretold this result before the block of ice was sectioned. In both tests, most of the ice was clear and glassy and there was a bottom layer which was white and opaque.

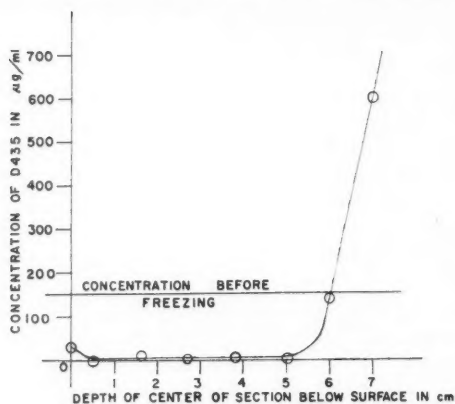


FIG. 4.

Figure 5 shows the concentration profile for ice VII. This is an example of the results obtained by freezing pure sodium chloride brine of concentration 35‰ (parts per thousand). In this case the freezing was done in a much deeper vessel so that the brine was initially 21.6 cm deep and the very high

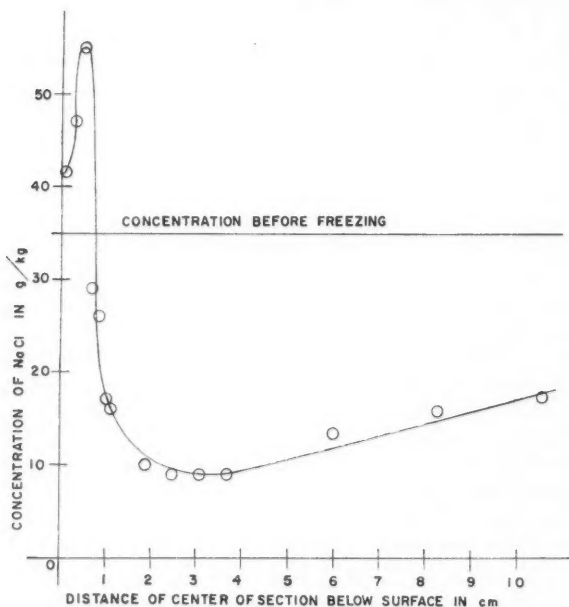


FIG. 5.

concentrations of salt found towards the bottom of the vessel after freezing do not appear over the depths here plotted. In this case also there was a transition layer clearly visible above the 1-cm level and the graph shows a corresponding concentration in the sodium chloride. There is, however, no evidence of a surface layer concentration.

Tests on ice frozen from melts containing D435 and ethylene glycol were undertaken to avoid the uncertainty of losses by evaporation, which are involved in the study of ice containing alcohol. Three concentration profile pairs are shown: for ice VIII (Fig. 6) the ambient freezing temperature was

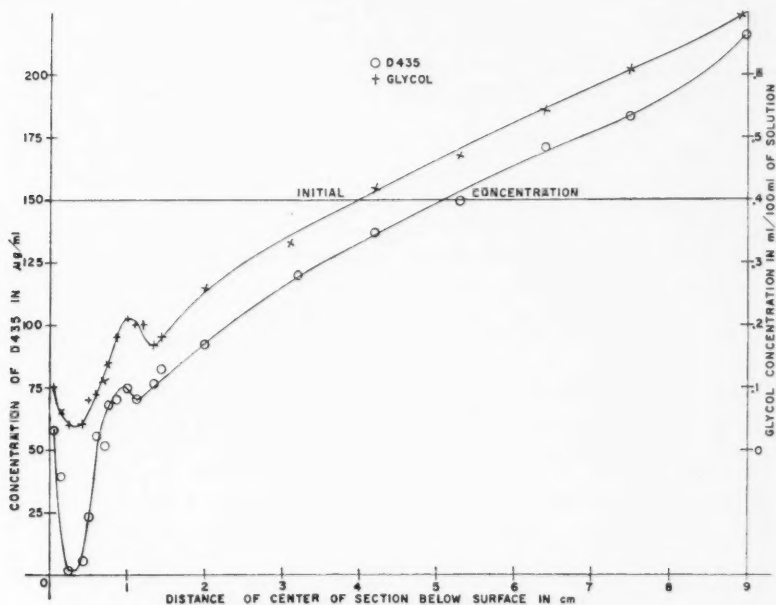
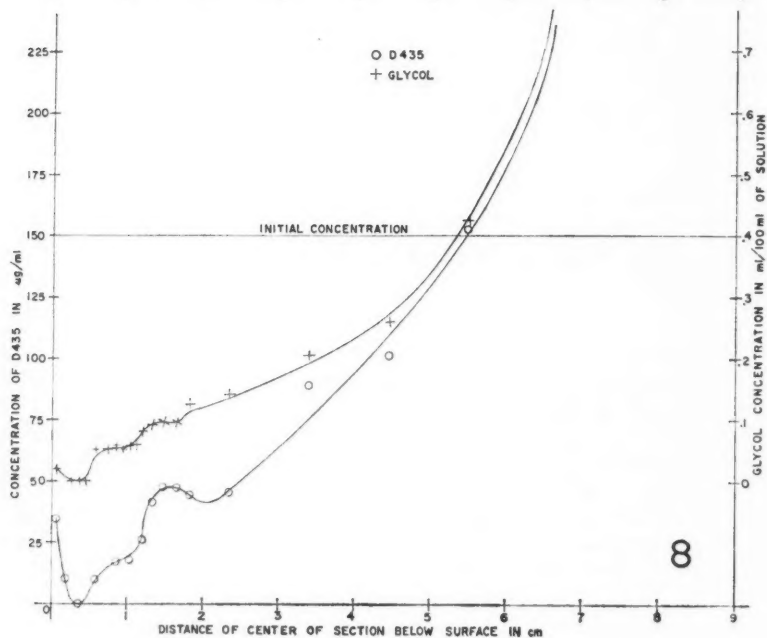
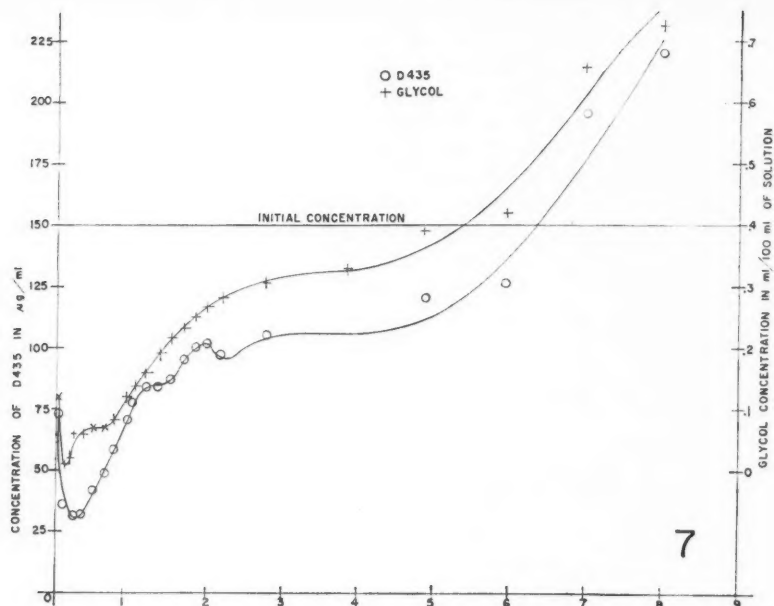


FIG. 6.

-28°C , for ice IX (Fig. 7) it was -19°C , and for ice X (Fig. 8) -5°C . As with the alcohol samples discussed previously, the D435 concentration follows closely that of the organic solvent, although the shape of these profiles differs considerably from those obtained in the alcohol tests. With alcohol the concentration throughout the bulk of the ice was uniform, whereas with glycol it rose more or less uniformly with depth. This indicates some rejection of glycol (and D435) by the ice, a rejection which is more pronounced when freezing takes place more slowly. In each of the three tests some glycol was expelled completely from the ice, remaining as a liquid film at the bottom of the vessel. The profiles all show evidence of a surface concentration and also of a transition layer, if not in the form of a concentration peak at least as a



FIGS. 7 AND 8.

change of slope in the curve. In ice IX and ice X the transition layer was observable visually in vertical sections through the blocks and was seen to be quite jagged. In the analysis of thin horizontal sections covering a fairly broad area this irregularity would have the effect of flattening the transition peak.

Visual examination of ice IX and ice X also showed patches of clear crystal growth surrounded by regions containing numerous air bubbles. It appears probable that thin sections may give erratic values in such non-uniform ice. This may account for points lying off smooth curves. Note that in Fig. 7 the same irregularities occur in both glycol and D435 concentrations.

To study possible evaporation losses, concentration measurements were made for a large number of samples of alcohol and water and of glycol and water, frozen in small cylindrical vessels (8 cm in diameter by 7.5 cm deep). Freezing was done with both covered and uncovered vessels, and in a number of the tests the surface layer of ice was removed repeatedly for analysis while freezing was proceeding.

These experiments showed that the first ice that forms on the surface of alcohol-water solutions is in the form of a fairly compact layer consisting of horizontal thin "sheets" which are well bonded together when the alcohol content of the solution is low (up to about 0.7%), but are weak and easily separated when the alcohol content of the solution is high (about 4% or more).

The alcohol content of this surface ice layer, and of successive ice layers that form after each in turn is removed, is lower than the average solution concentration and is surprisingly constant (about 0.4% with an initial concentration of 0.7%).

For closed vessels, analysis of the ice and of the unfrozen melt confirmed that no alcohol had been lost by evaporation. For open vessels the alcohol concentration of the surface ice does decrease slowly with time. (For example, two similar samples of ice were stored, with and without covers, in a cold room at -15°C for 1 week. The concentration of alcohol in the top 1-cm layer was then 3.23% and 2.90% respectively. Below about 1.5 cm the concentration remained alike in the two vessels.)

After the ice layer reaches a thickness of the order of 1 cm, the ice begins to grow in long pendent vertical plates. In these experiments, the plates were 1 to 1.5 cm in width, very thin (probably about 0.1 mm thick), and crystal clear. They were observed up to 3 or 4 cm in vertical length and were spaced about 0.5 cm apart, in groups at least roughly parallel. The alcohol concentration of these plates, strained from the solution (so that inevitably a little liquid adhered), did not differ from the value found for the surface ice layers.

When the solution is allowed to freeze completely, alcohol is extruded from the block and remains as a liquid film on the inside of the vessel.

The concentrations of alcohol found throughout the ice, when the sample was allowed to freeze completely, were somewhat higher than the concentrations found in ice formed on similar solutions, when only part of the melt was allowed to freeze. This is probably owing to the fact that horizontal layers cut from a solid block of ice contain both ice crystals and some concentrated alcohol solution trapped between them. The sections analyzed were

relatively thick, so that the fine detail of Fig. 3 was not obtained but the concentrations were consistent with the profiles of Fig. 3.

Melts containing glycol and water were frozen and analyzed in a similar fashion. The freezing pattern found was very much like that for alcohol-water mixtures; the horizontal layer and its pendent vertical plates contained equal concentrations of glycol, and this concentration was surprisingly similar, quantitatively, to that in the alcohol case. When glycol melts are frozen solid, however, the concentration profile below the 2-cm level is markedly different; comparing ice IV (Fig. 3) with ice VIII (Fig. 6) it is evident that below the transition layer the alcohol values remain constant throughout most of the ice, whereas the glycol values increase steadily with depth.

As the ice crystals form, both alcohol and glycol are rejected. But the alcohol, free to move between the pendent ice crystals, will tend to rise, since it is lighter than water, whereas the glycol being heavier than water will tend to sink. In the case of alcohol then, the rejection and gravity effects are in opposition, and throughout the bulk of the volume, measurements of the alcohol content of a horizontal layer give an almost constant value.

In the case of glycol, where the effects of rejection and gravity move the glycol in the same direction, the trapped solution in the lower layers will have a higher concentration than in those above.

Solutions containing water-soluble dyes (methylene blue, methyl violet, and eosin) were next investigated, with most striking results. When the solutions contained only a dye and water the dye was so strongly rejected as freezing proceeded that the ice was quite clear and colorless except at the bottom where the dye was concentrated in a sharply defined region. But when these solutions contained both dye and ethyl alcohol, the ice appeared to be uniformly colored throughout.

Examination of this ice was attempted under the microscope in the cold room. When sufficiently thin sections could be set up at the right angle, it was possible to see that the ice consisted of clear platelets of colorless ice separated by thin highly colored films.

DISCUSSION

The concentration profiles shown in this paper give strong evidence for a peak in concentration values at the position below the surface found by Perey and Pounder (1958) to be the position of a transition layer in the crystal structure. At this transition layer a rapid change occurs in both crystal sizes and orientations. In most of the ice samples tested a concentration peak was also found in the surface layer. The absolute size of this concentration is uncertain, because the value found in each case must be a function of the thickness of the layer of ice in which it was measured. The thinner the layer the higher was the measured concentration, suggesting that the concentration is a maximum in a very thin, possibly even monomolecular, surface film. The same argument applies to the value found for the transition layer peak, with an added complication. Visual examination of a vertical section usually showed the transition layer to be very thin but not in a horizontal plane. Sometimes

it was quite jagged, occasionally varying in depth by as much as half a centimeter. If the transition layer itself could be isolated, one would expect to find very much higher concentrations than any here recorded.

It has been shown that when pure aqueous solutions of sodium carboxymethyl cellulose (CMC), various water-soluble dyes, sodium chloride, ethylene glycol, and ethyl alcohol are frozen, the amount of solute trapped in the ice varies widely. For the concentrations and freezing rates used, the CMC and dyes are virtually completely rejected by the ice. Some salt is trapped; in Fig. 5 the region from about 2 to 6 cm in depth might be considered normal and shows that about 30% of the salt was retained in the ice. The concentrations of alcohol and glycol vary too much with depth to speak of a normal concentration but a reasonable guess is that 90% of the alcohol and possibly 50 to 60% of the glycol are trapped in the ice. These results suggest the possibility that the solubility in water of the additive is a factor—the CMC and the dyes are only slightly soluble in water compared to salt and the two organic liquids are infinitely soluble in water.

The freezing of solutions containing both alcohol (or glycol) and CMC (or a dye) is interesting, since the presence of the CMC does not appear to alter the distribution of the alcohol or glycol in the ice but the distribution of the CMC now conforms closely to that of the organic liquid. Apparently the CMC is carried by the alcohol or glycol to positions in the ice not available to pure CMC. By some physical or chemical process the small alcohol molecule (or possibly several of them) takes the huge CMC molecule "under its wing" and persuades the growing ice lattice to treat them approximately as equals. It is perhaps important to note that the number of alcohol molecules is greater by several orders of magnitude than that of CMC molecules, so that even if some of the alcohol enters into a chemical reaction there is plenty of it left to alter the refractive index of the solution. A possible chemical reaction is esterification of the CMC. Although esterification ordinarily reduces the solubility in water, this is not necessarily the case. Noller (1951, p. 303) points out that cellulose is insoluble in water because of strong van der Waals forces and proton bonding between chains. Etherification to CMC separates the chains because of the size of the carboxymethyl group and reduces these forces greatly. Possibly esterification of the CMC carries this process a step farther. A possible physical mechanism for retaining the CMC in the ice is through lattice defects. There is no evidence that alcohol can fit permanently into an ice lattice, but alcohol affects the properties of ice so markedly that it is tempting to suppose that alcohol can attach temporarily to a growing ice crystal, giving rise to imperfections in the lattice. If these imperfections are large the CMC molecules may be trapped in them, although not of course forming part of the lattice. The present experiments do not suggest which of these speculations is the more likely, or, indeed, if either of them is the correct explanation.

The results illustrated in Figs. 6, 7, and 8 show that the amount of solute trapped in the ice increases with the decrease in ambient temperature and hence increase in freezing rate. This result is well known in field studies of sea ice.

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REFERENCES

- ANDERSON, D. L. 1958. A model for determining sea ice properties. Arctic Sea Ice, Washington, NAS-NRC Pub. No. 598.
ASSUR, A. 1958. Composition of sea ice and its tensile strength. Arctic Sea Ice, Washington, NAS-NRC Pub. No. 598.
BLACK, H. J., Jr. 1951. Anal. Chem. **23**, 1792.
DREYWOOD, R. 1946. Ind. Eng. Chem. Anal. Ed. **18**, 499.
LOEWUS, F. A. 1952. Anal. Chem. **24**, 219.
MOKRASCH, L. C. 1954. J. Biol. Chem. **208**, 55.
NOLLER, C. R. 1951. Textbook of organic chemistry (W. B. Saunders, Philadelphia).
PEREY, F. G. J. and POUNDER, E. R. 1958. Can. J. Phys. **36**, 494.
POUNDER, E. R. 1958. Can. J. Phys. **36**, 363.
ROE, J. H. 1954. J. Biol. Chem. **208**, 889.
——— 1955. J. Biol. Chem. **212**, 335.
SCOTT, T. A. and MELVIN, E. H. 1953. Anal. Chem. **25**, 1656.

NEGATIVE RESISTANCE IN SEMICONDUCTOR DEVICES¹

RONALD E. BURGESS

ABSTRACT

Negative resistance can appear in the static and high-frequency characteristics of devices in which the current is determined by both voltage and temperature. The properties of the a-c. impedance arising from the interaction of thermal and non-thermal effects are discussed and criteria for the appearance of negative resistance over certain ranges of frequency are derived. The application of this analysis to devices which do and which do not exhibit isothermal negative resistance is considered. In an Appendix, a current-temperature relation depending on two activation energies is shown to provide a quantitative model for interpreting the observed turnover behavior of germanium diodes.

The appearance of "thermal turnover", i.e. a voltage maximum followed by a negative resistance region in the characteristics of semiconductor devices, has been discussed previously (Burgess 1955*a*, *b*, *c*). In the present paper the combination of thermal and voltage-controlled processes is considered generally and the results are applied to a discussion of the attainment of negative resistance. We exclude the effects obtained by transit time phenomena and also the spurious negative resistance which seemingly occurs in junction diodes under avalanche breakdown conditions and in fact arises from the voltage-controlled statistics of the breakdown process (Burgess 1959).

The voltage-controlled effects most commonly involved are: impact ionization leading to avalanche multiplication, carrier injection and extraction, space-charge-limited flow, internal field emission (or Zener effect), and non-linear carrier mobility in strong electric fields. Except in the simple case of an ohmic device at low electric fields, one or more of these effects will be present.

In general the current may be written $I = I(V, T)$ and the differential resistance r which is the small-amplitude a-c. resistance at zero frequency is given by

$$(1) \quad r = \frac{dV}{dI} = R \frac{1-y}{y+x}$$

where $R = V/I$ is the d-c. resistance, $x = R (\partial I / \partial V)_T$, $y = (V/K) (\partial I / \partial T)_V$, K = thermal conductance between device and ambient = $\partial(I V) / \partial T$.

The dimensionless quantities x and y are respectively the representative parameters of the isothermal characteristic at the operating temperature and the temperature coefficient of the current at the operating voltage.

The four alternating sectors of positive and negative differential resistance in the x - y plane are separated by the lines $y = 1$ and $x + y = 0$. The line $x = 1$ corresponds to devices which are linear in the isothermal condition (e.g. thermistors). Usually semiconductor devices will have positive values of y

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although in some exceptional cases such as those involving high electric fields it may be possible for y to be negative.

If x is positive then as the current through the device increases attainment of the condition $y = 1$ corresponds to voltage turnover ($r = 0$) after which negative resistance of the current-controlled type is obtained. When x and y are of the same sign the differential resistance must lie between $-R$ and $(\partial V/\partial I)_T$ and this indicates the limits of magnitude of the attainable negative resistance at any operating point beyond turnover.

It may also be inferred from equation (1) that in a diode whose isothermal reverse current does not saturate ($x > 0$) the differential resistance is smaller in magnitude (whether positive or negative) than in an otherwise identical diode exhibiting saturation. Thus avalanche multiplication sharpens the breakdown process compared with that due to thermal effects alone but conversely it reduces the attainable negative resistance beyond turnover.

In a diode displaying isothermal negative resistance ($x < 0$), as in the forward characteristic of narrow germanium junctions (Esaki 1958), the differential resistance is modified by thermal effects once y is no longer small compared with both 1 and $-x$. If thermal effects are sufficient for y to exceed $-x$ and $-x < 1$ then they will dominate over the Zener effect and produce thermal turnover of the voltage maximum type. Circumstances can arise in such a device in which the characteristic on proceeding from the origin could exhibit a current maximum followed by a current minimum followed in turn by a voltage maximum.

The above remarks about the characteristics apply to frequencies sufficiently low for the temperature always to be in a steady state with the applied power. At higher frequencies thermal inertia causes a lag in the temperature variation and the differential resistance derived from the static characteristic must be replaced by the complex impedance. If τ is the thermal time constant this impedance is derived by replacing the thermal conductance K by the complex thermal admittance $K(1+i\omega\tau)$ whence

$$(2) \quad Z(\omega) = R[1-y/(1+i\omega\tau)]/[x+y/(1+i\omega\tau)].$$

This function has a semicircular locus in the Z plane with the ends of the diameter on the resistance axis occurring at $Z(0) = r$ and $Z(\infty) = (\partial V/\partial I)_T$.

It is immediately seen that the criterion for thermal effects to be absent is not that $\omega\tau$ shall be large compared with unity but large compared with y and y/x .

The condition for negative resistance to appear is

$$(3) \quad x\omega^2\tau^2 < (y-1)(y+x).$$

From this inequality may be derived

(i) the upper frequency limit at which a device without isothermal negative resistance may display negative resistance due to thermal effects, or

(ii) the frequency below which isothermal negative resistance may be suppressed by thermal effects.

In a linear device ($x = 1$) the upper limit for a purely thermally derived negative resistance is simply

$$(4) \quad \omega\tau < (y^2 - 1)^{\frac{1}{2}}.$$

The presence of thermal effects introduces a reactive component into the impedance which is inductive if $y(1+x)$ is positive and capacitive if $y(1+x)$ is negative. This may be useful or embarrassing depending upon the manner in which the device is being used. An example of benefit occurs in very low-frequency oscillators using thermistors where the inductive reactance produced by the thermal inertia permits frequency control simply by shunting the thermistor with a pure capacitance (Burgess 1955c). Similar inductive behavior and oscillations in point-contact or junction germanium diodes are possible but here x is greater than unity due to avalanche multiplication so reducing the upper frequency limit for negative resistance to appear (equation (3)).

In any given circumstances the effective time constant differs from τ to an extent which depends on x and y and also on the external circuit so that the dynamic behavior can only be evaluated by considering the complete system.

One type of dynamic behavior of practical importance is the switching time of a bistable negative resistance device between two stable points. The transition involved is essentially of large amplitude embracing the whole of the negative resistance region and is thus outside the scope of the present small-amplitude theory. However, there is still validity in the observation that the switching time is not simply related to τ even when it is determined by thermal inertia, since x and y and the external circuit determine the fashion in which the variations of current, voltage, and temperature are interrelated.

Thermally produced negative resistance is commonly associated with relatively long relaxation times of the order of milliseconds. If, however, the current-controlling region is of small dimensions and material has a high thermal diffusivity (especially true at low temperatures) the thermal time constant can easily be less than a microsecond. Conditions of this type obtain for instance in the contact region of a point-contact diode.

Furthermore it must be stressed that the upper frequency limit for negative resistance to occur may be appreciably greater than the plausible value $1/2\pi\tau$. In conditions where the temperature control of the current is sharp, y can be much greater than unity; if for instance $y = 100$ and $x = 5$ then it is found from equation (3) that $f_{\max} = 7/\tau$. In this type of situation it is seen by reference to equation (2) that the heat capacity τK and not the thermal conductance K is important.

It is possible, though not yet conclusive, that the negative resistance (McWhorter and Rediker 1959) and oscillations (Koenig and Brown 1959) observed in germanium filaments at low temperatures have thermal origin. The latter authors have suggested that the negative temperature coefficient of the breakdown field associated with impact ionization leads to a local thermal instability of some small region of the filament. The former pair of authors point out that a switching time of 2×10^{-9} second is possible in the negative resistance region. As was remarked above the thermal time constant

will not be as small as this switching time when the parameter y is large compared with unity and, indeed, it is in this phenomenon.

Even in devices with long thermal time constants or those used at frequencies high enough for thermal effects to be unimportant the behavior of the low-frequency differential resistance given by equation (1) is still of importance as it determines the d-c. and low-frequency stability of the device in conjunction with the associated d-c. bias circuit and it must be heeded to obtain monostable operation free from low-frequency oscillations.

In the discussion above, the only inertial process considered was thermal and the isothermal admittance was assumed to be real and frequency independent and equal to the slope of the isothermal characteristic at the operating point.

The treatment can be generalized by replacing $(\partial I/\partial V)_T$ by $Y(\omega, T)$ which is the small-amplitude admittance at ω and at fixed temperature T . The impedance of the device including thermal effects then becomes

$$(5) \quad Z(\omega) = \frac{(1-y) + i\omega\tau}{(1+i\omega\tau)Y + (y/R)}$$

which behaves as $1/Y$ for frequencies sufficiently high for $\omega\tau \gg |1-y|$ and $|y/R|$.

The condition for negative resistance to occur becomes

$$(6) \quad G\omega^2\tau^2 + (1-y)(G+y/R) + B\omega\tau y < 0$$

where $Y = G + iB$.

At high frequencies where the isothermal admittance may become complex as considered above it is also necessary to examine the parameter y which is determined by $(\partial I/\partial T)_V$. Here I denotes the total current through the device and y is real only if the current variation at constant voltage is cophasal with the temperature variation producing it. This would not be the case, for instance, when the capacitive component of current is temperature modulated by variation of the permittivity of the material or the geometry of a space-charge region. Hence when Y becomes complex at high frequency account must be taken of y also becoming complex though with a phase angle which will in general differ in magnitude and even in sign from that of y .

An important example of a class of semiconducting material in which y is complex and furthermore the temperature coefficient of conductivity is negative occurs in ferroelectric crystals near the Curie point. For instance, barium titanate can be made semiconducting by adding cation impurities of suitable valency (Saburi 1959), and the resulting material can have room temperature resistivity in the range $10-10^4$ ohm cm. At the Curie point an increase of 5° in temperature may produce a 100-fold increase of resistivity corresponding to a temperature coefficient of conductivity of -1 deg^{-1} . Thermistors constructed from such materials would have very large negative values of y ; for example, if the applied power causes a 10° rise of temperature above the ambient $y = -10$.

In such a ferroelectric material near the Curie point the temperature coefficient of the permittivity would be large and thus y would be significantly complex. For we have

$$\left(\frac{\partial I}{\partial T}\right)_V \propto \left[\frac{\partial(\sigma + i\omega\epsilon)}{\partial T}\right]_E$$

with both $\partial\sigma/\partial T$ and $\partial\epsilon/\partial T$ negative. The comparison of $(\partial\epsilon/\partial T)/(\partial\sigma/\partial T)$ with the thermal time constant τ determines the importance of the ferroelectric behavior in modifying the dispersive properties of the impedance.

APPENDIX

THERMAL TURNOVER IN THE TWO-ACTIVATION-ENERGY MODEL

In a germanium diode the consistently observed decrease of turnover power with increasing ambient temperature proves to be exacting in the construction of a satisfactory phenomenological model for the characteristics. The suggestion (Cutler 1957) that a current-temperature dependence based on a process involving two activation energies is here shown to yield the correct behavior but with an interpretation of the experimentally derived parameters which differs from that commonly used.

Consider a current I of the form

$$I = F(V) [A \exp(-a/T) + B \exp(-b/T)]$$

where $a > b$ and correspondingly $A > B$. The dependence of current on temperature T at constant voltage when plotted logarithmically against $1/T$ will display two asymptotic linear regions with a slope $-b$ at low temperature and $-a$ at high temperature and intersecting at a temperature T_0 where the two components of current are equal:

$$T_0 = (a-b)/\ln(A/B).$$

Now under steady-state operation and for linear thermal conduction the device temperature T and ambient temperature T_a are related by

$$K(T - T_a) = IV$$

where K is the thermal conductance between the current-controlling region of the device and the ambient.

The turnover condition ($dV/dI = 0$) is independent of $F(V)$ and given by $y = 1$ or

$$I_1 V_1 / K = T_1 - T_a = T_1^2 / S(T_1)$$

where suffix 1 denotes the values at turnover and S is the slope function given by

$$S(T) = \frac{Aae^{-a/T} + Bbe^{-b/T}}{Ae^{-a/T} + Be^{-b/T}} = -\frac{d(\ln I)}{d(1/T)}.$$

For turnover to occur $S > 4T_a$ is necessary.

The function S has the value b at low temperatures, and a at high temperatures, and $\frac{1}{2}(a+b)$ at T_0 where to a close approximation dS/dT reaches its maximum value.

The dependence of the turnover power ($P_1 = I_1 V_1$) on the ambient temperature is found from

$$\frac{dP_1}{dT_a} = K \left[\frac{dT_1}{dT_a} - 1 \right] = K \left[\left(1 - \frac{2T_1}{S_1} + \frac{T_1^2}{S_1^2} \frac{dS_1}{dT_1} \right)^{-1} - 1 \right].$$

In germanium diodes this quantity is found experimentally to be negative over an extensive range of temperature.

For this to be possible

$$\frac{dS_1}{dT_1} > \frac{2S_1}{T_1}.$$

The most favorable temperature for this to be realized is close to $T_1 = T_0$ for which the inequality becomes

$$\ln \frac{A}{B} > 4 \frac{a+b}{a-b}.$$

This condition does not depend on the thermal conductance K and is determined only by the two ratios A/B and a/b .

Introducing the parameter

$$C = [(a-b)^2/2(a+b)T_0] - 2 = \frac{1}{2} \frac{a-b}{a+b} \ln \frac{A}{B} - 2$$

which must be greater than zero for the above inequality to hold, we have the following results in the condition $T_1 = T_0$:

$$dT_1/dT_a = [1 + 2T_0C/(a+b)]^{-1},$$

$$P_1 = K(T_0 - T_{a0}) = KT_0^2/S_0 = 2KT_0^2/(a+b),$$

$$T_{a0} = T_0 - T_0^2/S_0 = T_0 - 2T_0^2/(a+b),$$

$$\frac{dP_1}{dT_a} = - \frac{KC}{C + (a+b)/2T_0}.$$

Thus the intercept of the tangent at T_{a0} to the (P_1, T_a) plot on the T_a axis is

$$\begin{aligned} T_1 &= T_{a0} - P_1/(dP_1/dT_a) \\ &= T_0(1 + 1/C). \end{aligned}$$

It is this intercept temperature which in the literature (Benzer 1949; Yamaguchi and Hamakawa 1959*a, b*) has been identified erroneously with the contact temperature or with the temperature at which the onset of intrinsic conduction occurs. In fact the intercept is larger than the contact temperature by the fraction $1/C$ (which may typically lie between 0.1 and 0.3) and has no relation to intrinsic conductivity. Similarly the slope dP_1/dT_a is usually much less than K whereas it is often assumed to provide a direct measurement of the thermal conductance.

Typical values for a germanium diode are:

$$\begin{aligned} A/B &= e^{20}, & a &= 8000^\circ, & b &= 2000^\circ, & \text{giving} \\ T_0 &= 300^\circ, & T_{a0} &= 282^\circ, & T_1 &= 375^\circ, & C &= 4, \end{aligned}$$

and

$$(dP_1/dT_a)_{T_1=T_0} = -0.19K.$$

It will be noted that the thermal conductance K in no way affects the temperature relations as it only appears in expressions involving the power. Furthermore the value of b is not of great influence on the results and it could be zero (corresponding to a current component independent of temperature) and yield the same qualitative features as for a non-zero value.

REFERENCES

- BENZER, S. 1949. *J. Appl. Phys.* **20**, 804.
BURGESS, R. E. 1955a. *Proc. Phys. Soc. B*, **68**, 766.
——— 1955b. *Proc. Phys. Soc. B*, **68**, 908.
——— 1955c. *J. Electronics*, **3**, 297.
——— 1959. *Can. J. Phys.* **37**, 730.
CUTLER, M. 1957. *IRE Trans. on Electron Devices*, **ED-4**, 201.
ESAKI, L. 1958. *Phys. Rev.* **109**, 603.
KOENIG, S. H. and BROWN, R. D. 1959. *J. Phys. Chem. Solids*, **10**, 201.
MCWHORTER, A. L. and REDIKER, R. H. 1959. *Proc. IRE* **47**, 1207.
SABURI, O. 1959. *J. Phys. Soc. Japan*, **14**, 1159.
YAMAGUCHI, J. and HAMAKAWA, Y. 1959a. *J. Phys. Soc. Japan*, **14**, 15.
——— 1959b. *J. Phys. Soc. Japan*, **14**, 232.

THE ELECTRICAL RESISTANCE OF DILUTE MAGNESIUM AND ALUMINUM ALLOYS AT LOW TEMPERATURES¹

F. T. HEDGCOCK, W. B. MUIR, AND E. WALLINGFORD

ABSTRACT

Experimental data on the influence of type and concentration of impurity on the low-temperature resistance of the metals, magnesium and aluminum, is presented. In particular, comparison is made of the electrical behavior of alloys formed using transition element impurities in the divalent metal magnesium, and in the trivalent metal aluminum with the behavior of similar impurities in some of the noble metals.

1. INTRODUCTION

The electrical resistance minimum in metals was discovered 25 years ago in gold by de Haas and van den Berg (1934), and since that discovery a considerable number of pure metals and alloys have been investigated for similar low-temperature anomalies. Most of these experimental studies have involved the noble metals and their alloys. At present some order is beginning to emerge from systematic investigations of the influence of type and concentration of impurity on the temperature of occurrence and relative size of the resistive anomaly.*

Electrical resistance minima in magnesium were first reported by Meissner and Voigt (1930) and later work by MacDonald and Mendelssohn (1950), Garfunkel, Dunnington, and Serin (1950), Thomas and Mendoza (1952), and Spohr and Webber (1957) confirmed these observations. Reports of an electrical resistance minimum occurring in aluminum (Keesom 1933) were not confirmed in later measurements made by Boorse and Niewodniczanski (1936), Garfunkel, Dunnington, and Serin (1950), and later by Thomas and Mendoza (1952). Although low-temperature resistive anomalies have been reported in magnesium and aluminum, no detailed study of the influence of type and concentration of impurity on the minimum has been carried out. Interest in this laboratory in the magnetic properties of magnesium and aluminum prompted an investigation of the electrical properties of a number of dilute alloys of magnesium and aluminum at low temperatures and we wish to report briefly on these measurements.

¹Manuscript received November 2, 1959.

Contribution from the Department of Physics, University of Ottawa, Ottawa, Ontario. Some of this research will be included in theses by W. B. Muir and E. Wallingford to be submitted in partial fulfillment for the Ph.D. and M.Sc. degrees, respectively, at the University of Ottawa. A preliminary report on the magnesium alloys was presented at the June meeting of the Canadian Association of Physicists held at McMaster University, Hamilton, Ontario, 1958.

*For a comprehensive review article and list of references, see "Electrical conductivity of metals and alloys at low temperatures" by D. K. C. MacDonald, *Handbuch der Physik*, Vol. XIV, Springer-Verlag, Berlin (1956).

2. EXPERIMENTAL METHOD AND SPECIMEN PREPARATION

2.1 Apparatus

The low-temperature cryostat is similar to the helium desorption unit described by Rose-Innes and Broom (1956) and will not be described here. With freshly activated charcoal in the desorption unit, a temperature run from 4.2 to 30° K could be made very slowly, the run usually taking from 4 to 5 hours. This meant that a number of resistance specimens could be run at one time. All temperatures above 4.2° K were measured with a Simon-type gas thermometer. Relative temperatures could be measured with an accuracy of better than 0.3% whereas the absolute temperature in the higher temperature regions should be within 1%. Between 2 and 4.2° K the temperature was determined using the known vapor-pressure scale. Temperature agreement between the gas thermometer and vapor-pressure measurements was better than 0.2%.

A current-potential method was used to measure the resistance of the samples. Pressed contacts were used and were either of screw- or knife-edge design. The voltages were measured with a galvanometer amplifier as described by MacDonald (1956). Scatter in the experimental points (due to electrical noise and stray thermal voltages) permitted the resistance ratios of the aluminum alloys to be determined with an accuracy of at least 0.5% whereas the magnesium alloys which exhibited large anomalies were not measured to better than 1%.

2.2 Magnesium Specimen Preparation

The alloys were made by Dow Chemical Company metallurgical laboratories and supplied as either chill-cast ingots or 0.25-in. rods. The resistance specimens were made by hot-rolling* the ingots at 400° C into strips approximately 0.005-in. thick and cutting these strips into wires of rectangular cross section. After fabrication, the samples were annealed at 450° C for 48 hours in an atmosphere of helium gas. Table I lists the alloys investigated and their resistance ratios $R_{4.2}/(R_{300}-R_{4.2})$. All of the alloys show a resistance ratio higher than the pure stock so that, if not all, at least some of the impurity is in solution. That alloys had been made in the case of magnesium-manganese and magnesium-iron systems can be seen in Table I where the resistance ratios show an approximate linear increase with nominal impurity content. Hot-rolling of sample 732 produced extremely large impurity gradients in the samples so that values for this specimen given in Table I are to be thought of as averages. The room-temperature resistivity of alloys 702, 730, 731 are 4.62×10^{-6} ohm-cm, 4.67×10^{-6} ohm-cm, and 4.82×10^{-6} ohm-cm, respectively, and are in good agreement with the published values of Salkovitz, Schindler, and Kammer (1957) for these concentrations and type of solute. Micrographic examination of the alloys showed a one-phase system with a minimum of oxide present.

*We are indebted to the Department of Mines, Ottawa, for carrying out the hot-rolling.

TABLE I
Spectrographic analyses and electrical properties of magnesium alloys

Alloy No.	Al	Ca	Cu	Fe	Mn	Ni	Pb	Si	Sn	Zn	Sb	Major impurity	$T_{min}, ^\circ K$	$R_{1,2}/(R_{100}-R_{4,2})$
728	<.001	<.01	<.001	<.001	<.001	<.0005	<.001	<.001	<.01	<.001	—	Pure	—	3.6×10^{-3}
87812	<.002	<.01	<.001	<.001	<.005	<.0005	<.001	<.007	<.01	<.004	—	Mn	7.0	18.2×10^{-3}
87813	<.003	<.01	<.001	<.001	.019	<.0005	<.001	<.009	<.01	<.006	—	Mn	10.0	24.1×10^{-3}
87814	<.003	<.01	<.001	<.001	.038	<.0005	<.001	<.010	<.01	<.003	—	Mn	10.8	26.7×10^{-3}
729	<.001	<.01	<.001	<.001	.041	<.0005	<.001	<.001	<.01	<.001	—	Mn	12	36.1×10^{-3}
732A	<.001	<.01	<.001	<.001	.042	<.0005	<.001	<.001	<.01	<.001	—	Mn	13	53.7×10^{-3}
732B	<.001	<.01	<.001	<.001	.042	<.0005	<.001	<.001	<.01	<.001	—	Mn	13.7	87.0×10^{-3}
702	<.0005	<.01	<.001	<.0009	<.0005	<.0005	<.001	<.001	<.001	.02	—	Zn	—	8.54×10^{-3}
730	<.001	<.01	<.001	<.001	<.001	<.0005	<.001	<.001	.035	<.001	—	Sn	—	10.2×10^{-3}
731	<.001	<.01	<.001	<.001	<.001	<.0005	<.001	<.001	<.01	<.001	.07	Sb	—	19.4×10^{-3}
757-3	<.001	<.01	<.001	.013	<.001	<.0011	<.001	<.001	<.01	.039	—	Fe + Zn	6.0	14.2×10^{-3}

2.3 Aluminum Alloy Preparation

The aluminum alloys were prepared by the Aluminum Company of Canada and a spectrographic analysis of these alloys is shown in Table II. The aluminum samples were cold-rolled to the same size as the magnesium alloys and usually given a strain-relieving anneal for 24 hours at 300° C in an atmosphere of helium prior to making measurements. Table II also shows the resistance ratios for the aluminum alloys as a function of nominal impurity content. It should be pointed out that some difficulty was experienced in keeping the iron in solution. The maximum solubility of iron in aluminum at 620° C is 0.035 wt.%.⁹ In order to put as much iron in solution as possible, the samples were quenched from 620° C after having received an homogenizing anneal at this temperature for approximately 24 hours. The purpose of this anneal was to try and remove the large impurity gradients that existed in the original ingots. An estimate of the gradient that existed in the original ingot may be seen in Table II where measurements of the resistance ratio

TABLE II
Spectrographic analyses and electrical properties of aluminum alloys

Alloy No.	Cu	Fe	Mg	Mn	Si	Major impurity	$R_{4.2}/(R_{300} - R_{4.2})$
GKP	< .002	< .002	< .002	< .001	< .001	Pure	3.0×10^{-3}
GKM	< .002	< .003	< .002	.011	< .001	Mn	18.5×10^{-3}
GKN	< .002	< .004	< .002	.053	< .001	Mn	68.2×10^{-3}
GKO	< .002	< .003	< .002	.082	< .001	Mn	111.5×10^{-3}
GKK	< .002	.05	< .002	< .001	< .001	Fe	25.0×10^{-3}
GKL	< .002	.11	< .002	< .001	< .001	Fe	$\begin{cases} 24.7 \times 10^{-3} \\ 16.4 \times 10^{-3} \end{cases}$

are given for each end of the GKL ingot which contains a nominal impurity content of 0.11% iron.

3. EXPERIMENTAL RESULTS

3.1 Electrical Resistance of Magnesium Alloys

A series of temperature-resistance runs on magnesium are shown in Fig. 1. Sample 728 is the pure material and exhibited no resistance minimum. Sample 727-1 is an iron alloy which presumably has too small a minimum to be detected with the present method of measurement. Alloy 757-3 has both iron and zinc present and the minimum is presumably due to the presence of iron. None of the alloys listed in Table I containing major impurities of zinc, tin, or antimony exhibited a resistance minimum. The rest of the alloys in Fig. 1 are magnesium-manganese alloys. The depth of the minimum is extremely large in sample 732 and much is larger than any reported for magnesium by previous authors (see above). Both the depth of the minima and the temperature at which the minima occur (T_{min}) increase with increasing impurity content. Using the resistance ratio as defined in Table I as a measure

*We are indebted to Mr. G. Marchand of the Aluminum Laboratories for making the phase diagram of aluminum-iron available to us.

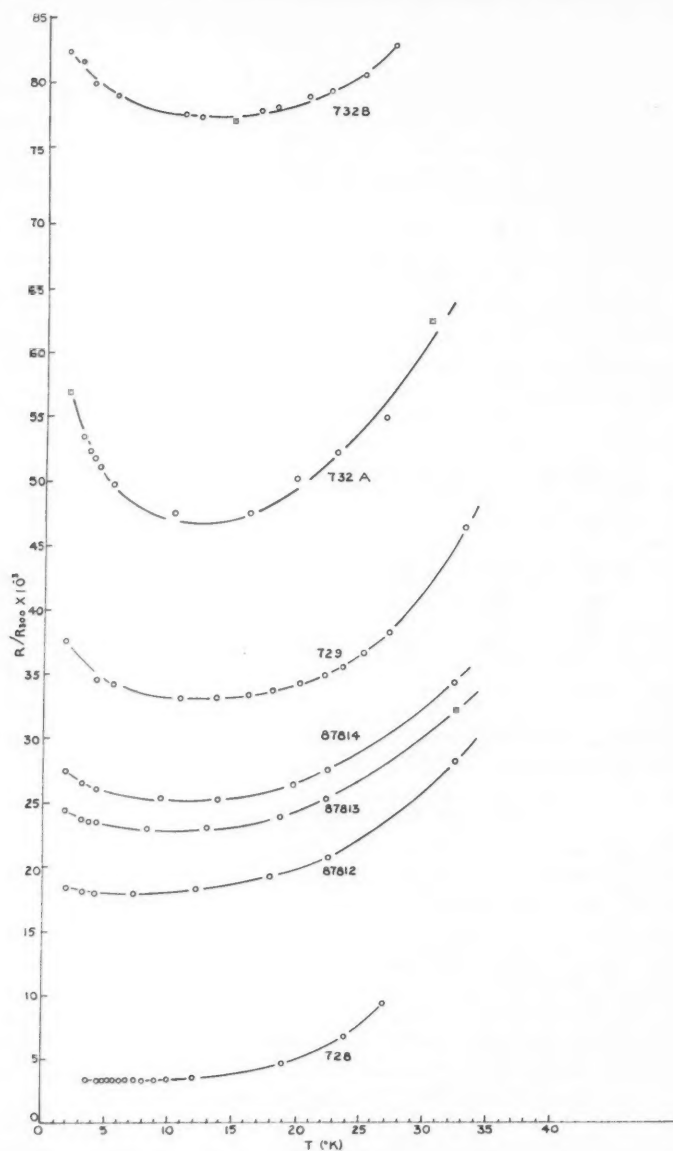


FIG. 1. Temperature dependence of the relative resistance of a number of magnesium alloys described in Table I.

of the impurity concentration, Fig. 2 shows a graph of T_{\min} and the normalized depth of the minima as a function of impurity content. The behavior of both of these parameters is similar to that described for certain copper alloys by MacDonald and Pearson (1955).

3.2 Electrical Resistance of Aluminum Alloys

Figure 3 shows the temperature dependence of relative resistance of some of the aluminum-manganese and aluminum-iron alloys described in Table II. None of these alloys exhibit a low-temperature resistive anomaly.

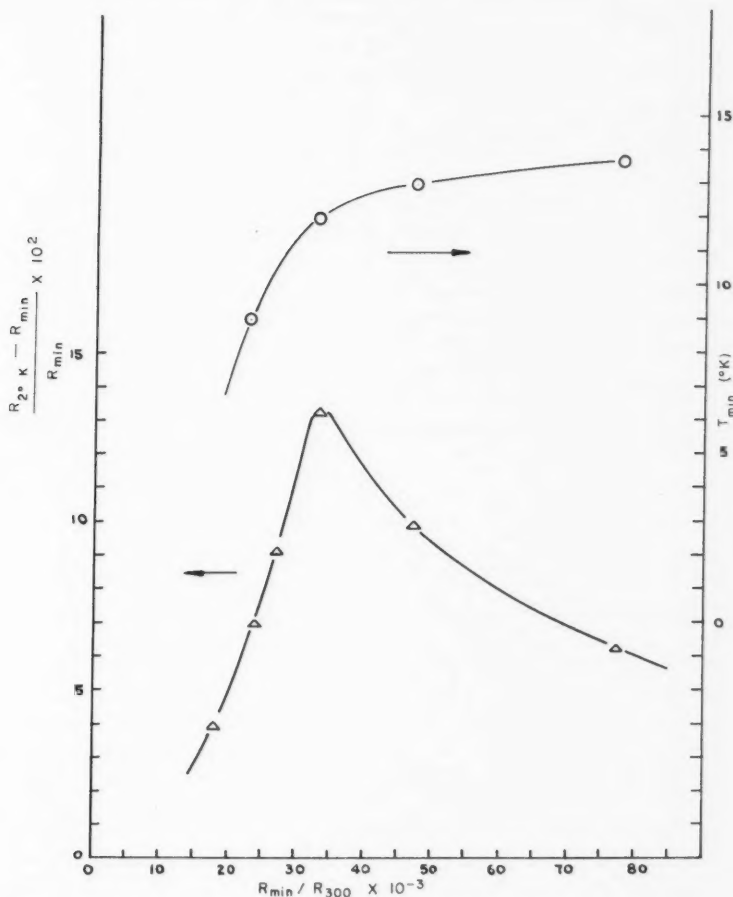


FIG. 2. Temperature of occurrence and the normalized depth of the resistance minimum occurring in magnesium as a function of impurity content.

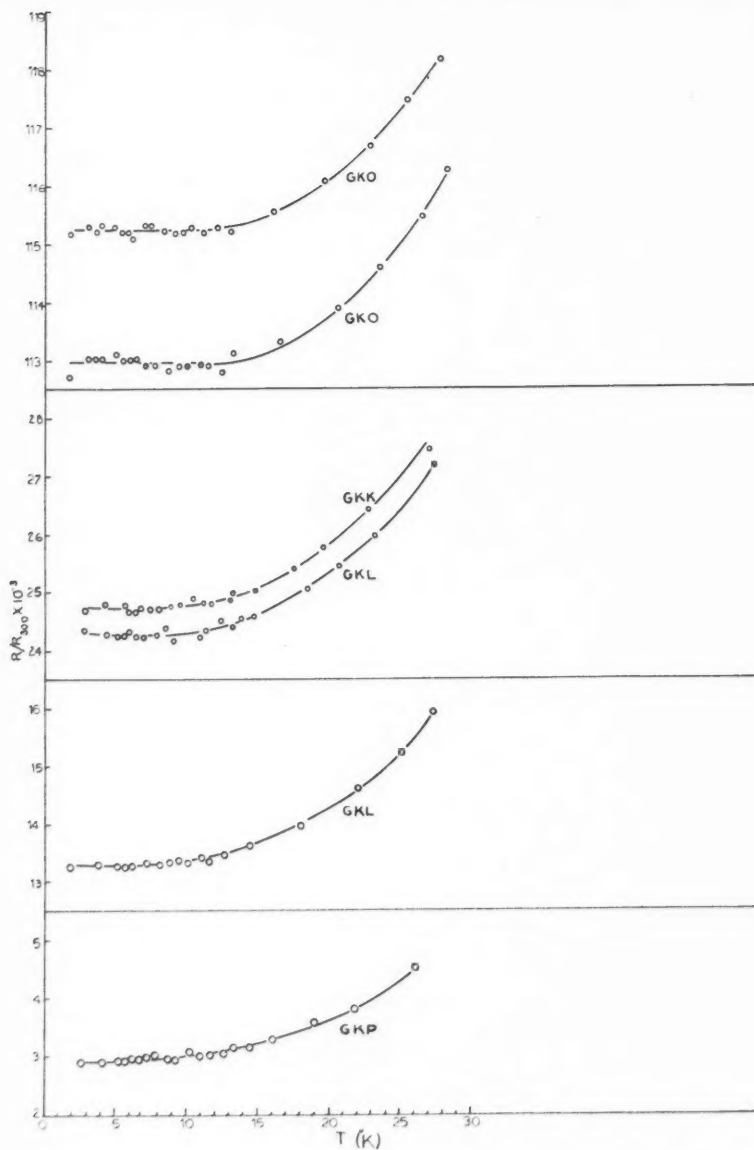


FIG. 3. Temperature dependence of the relative resistance of a number of aluminum alloys described in Table II.

3.3 Room Temperature Resistivity and Residual Resistance of the Magnesium and Aluminum Alloys

Mathiessen's rule states that if the total resistivity of an alloy is considered to consist of a thermal component which is the same as in the pure solvent (ρ_m) and a temperature independent contribution due to scattering from impurity ions (ρ_0), then the total resistivity can be written

$$\rho = \rho_m(T) + \rho_0.$$

Although the statement is of limited value, it is suggested that since all of the resistance temperature curves approach parallelism above the region where impurity scattering dominates the present alloy, systems may be said to obey the Mathiessen rule approximately.

Nordheim (1931), assuming the Mathiessen rule, and using a first-order perturbation calculation, has shown that if the electron concentration and structural properties of the base metal are not modified on alloying, then for low concentrations of solute ($<1\%$) ρ_0 (and hence ρ) should increase linearly with concentration. Using the data in Tables I and II it may be seen that the Nordheim rule is not obeyed well for these very dilute alloys. As has been discussed previously by MacDonald and Pearson (1955), the nominal composition of dilute alloys often bears very little relation to the amount of impurity in solution and for this reason the resistance ratio is a more reliable indication of the actual amount of impurity dissolved.

Values of the room-temperature resistivity for pure magnesium (alloy 728) and pure aluminum (alloy GKP) are 4.66×10^{-6} ohm-cm, and 2.77×10^{-6} ohm-cm respectively. Both the values of room-temperature resistivity and resistance ratio for the pure metals aluminum and magnesium are in good agreement with the most recent values reported by Thomas and Mendoza (1952) and Salkovitz *et al.* (1957).

4. CONCLUSION

Five general conclusions may be drawn from the alloy systems of magnesium and aluminum studied so far:

- (i) No sample of nominally pure magnesium showed a resistance minimum within the accuracy of the present measurements.
- (ii) Only the transition elements, manganese and iron, appear to induce a minimum in magnesium, manganese being the more effective of the two. Solutes such as antimony, zinc, and tin do not cause a minimum.
- (iii) The resistance maximum that manganese induces in copper, gold, and silver (see MacDonald's article, 1956) at temperatures lower than the minimum is not induced in magnesium above a temperature of 2° K.
- (iv) The concentration and temperature dependence of the minimum in the magnesium-manganese system exhibits behavior similar to that of the copper alloys with B group solutes gallium, indium, germanium, and tin studied by MacDonald and Pearson (1955). It seems reasonable to conclude therefore that the general behavior of the resistance minimum in a divalent

metal such as magnesium is similar to the behavior of the minimum in a monovalent metal such as copper containing a B group solute.

(v) The present results made on a more complete set of alloys than those previously studied are in agreement with the conclusion of Thomas and Mendoza (1952) that the transition elements iron and manganese do not induce a minimum in aluminum.

ACKNOWLEDGMENTS

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REFERENCES

- BOORSE, H. A. and NIEWODNICZANSKI, H. 1936. *Proc. Roy. Soc. A*, **153**, 463.
GARFUNKEL, M. P., DUNNINGTON, F. G., and SERIN, B. 1950. *Phys. Rev.* **79**, 211.
DE HAAS, W. J. and VAN DEN BERG, G. J. 1934. *Physica*, **1**, 1115.
KEESOM, W. H. 1933. *Commun. Kamerlingh Onnes Lab. Univ. Leiden*, No. **224**, C.
——— 1934. *J. Phys. Radium*, **5**, 373.
MACDONALD, D. K. C. and MENDELSSOHN, K. 1950. *Proc. Roy. Soc. A*, **202**, 523.
MACDONALD, D. K. C. and PEARSON, W. B. 1955. *Acta Metallurgica*, **3**, 392, 403.
MEISSNER, W. and VOIGT, B. 1930. *Ann. Physik (Leipzig)*, **7**, 761.
NORDHEIM, V. L. 1931. *Ann. Physik*, **9**, 641.
ROSE-INNES, A. C. and BROOM, R. F. 1956. *J. Sci. Instr.* **33**, 31.
SALKOVITZ, E. J., SCHINDLER, A. I., and KAMMER, E. W. 1957. *Phys. Rev.* **105**, 887.
SPOHR, D. A. and WEBBER, R. T. 1957. *Phys. Rev.* **105**, 1427.
THOMAS, J. G. and MENDOZA, E. 1952. *Phil. Mag.* **43**, 900.

THE ASSOCIATION OF VISIBLE AURORAL FORMS WITH RADAR ECHOES¹

G. F. LYON

ABSTRACT

A peak in 48.2-Mc/sec echo occurrence is observed at Saskatoon corresponding in time to the period of breakup of quiet arcs into active rayed structures. This is also the time of most frequent occurrence of characteristic "curl" forms in the aurora. If, as Gartlein suggests, the "curl" forms are formed by instabilities in a sheet beam then the primary particles are positively charged.

INTRODUCTION

Many observers have noted a close statistical correlation between the occurrence of very high frequency radar echoes and visible aurora. Little, Rayton, and Roof (1956) have summarized much of the previous work and concluded that the radio wave scatterers are closely associated in space and in time with visual aurora, but that because of aspect sensitivity, only aurora occurring at low elevation angles toward the north as seen from the radar station may be expected to give echoes. In general, auroral forms at elevation angles below about 15° will appear to consist of quiet arcs or diffuse forms, whereas the same aurora when viewed near the zenith may exhibit more structure and motion. Thus because the radio-observing site must be some 500 km from the scattering region, zenith observations of the visible form corresponding to a given radar echo are rarely obtained and few workers have attempted to correlate radio echoes with specific visible forms. Currie, Forsyth, and Vawter (1953) at Saskatoon, using simultaneous camera and radar observations from the same site, noted that echoes were usually observed from moderately bright aurora showing some structure and that structure was apparently a more important criterion for echo occurrence than luminosity.

During a recent radar investigation of auroral motions (Lyon and Kavadas 1958) carried out at Saskatoon (latitude 52.1° N., longitude 106.6° W.), an excellent statistical correlation was obtained between echo occurrence and the occurrence of visible aurora as recorded on an I.G.Y. all-sky camera situated at Flin Flon (latitude 54.8° N., longitude 101.8° W.), approximately under the scattering region. This paper concerns an attempt to detect a more detailed correlation between echo occurrence and specific visible auroral forms as observed on the Flin Flon camera.

OPERATIONAL DETAILS

The radar frequency was 48.2 Mc/sec and the radar was in operation during the period January 18 to April 28, 1958. The equipment has been described in a previous paper (Lyon and Kavadas 1958).

¹Manuscript received November 17, 1959.

Contribution from the Institute of Upper Atmospheric Physics, University of Saskatchewan, Saskatoon, Saskatchewan.

A detailed study was possible only when certain conditions were all fulfilled, namely that (1) the radar was operating, (2) the camera was not obscured by cloud or snow, (3) visible aurora occurred, and (4) the picture quality was such as to permit identification of the auroral form. These conditions were all fulfilled on 33 nights during the period under investigation. For analysis each night was divided into 10-minute periods. In all there were 910 periods in which visible aurora was present. This was considered to be a sufficient number to allow statistical treatment.

The useful field of view of the camera at Flin Flon covered the ranges between 350 km and 650 km from the radar at Saskatoon. Few echoes were received from ranges less than 350 km. Some echoes were received from ranges greater than 650 km and in these cases the form of the visible aurora beyond the camera was taken to be the same as that within the camera field of view. Most of the echoes were received from ranges within the camera field. No attempt was made to correlate the visible aurora and the echoes exactly in range as usually the form present at the exact echo range was also present at lesser and greater ranges at the same time.

RESULTS

1. Echo-Visible Form Correlation

In general, the pattern of the visible aurora for any one night followed that described by Heppner (1954). The form before local midnight was usually a quiet arc and the form after midnight was usually an active form, often exhibiting a rayed structure. During the period around midnight in which the breakup of arcs into rayed structures occurred, the intermediate form which most often developed was that of an arc with a "curl" or spiral discontinuity. A typical camera record of an arc with a "curl" is shown in Fig. 1.

For the purpose of analysis the visible aurora was divided into three main groups, namely:

- (a) quiet arcs,
- (b) arcs with a "curl" or spiral discontinuity,
- (c) active rayed structures.

On this basis the form present in any one 10-minute period was recorded. The radar records were then analyzed using the same 10-minute periods as had been used for the camera records. An echo occurring in any one period was associated with the visible form in the same period as displayed in Table I.

TABLE I
Echo-form correlation

	No. of 10-minute periods			Percentage of visible form giving echoes
	Visible aurora	Echoes	No echoes	
Quiet arcs	365	18	347	5
Curls	174	54	120	31
Rayed structures	371	52	319	14
No aurora	—	4	—	—
Total	910	124	786	14

PLATE I

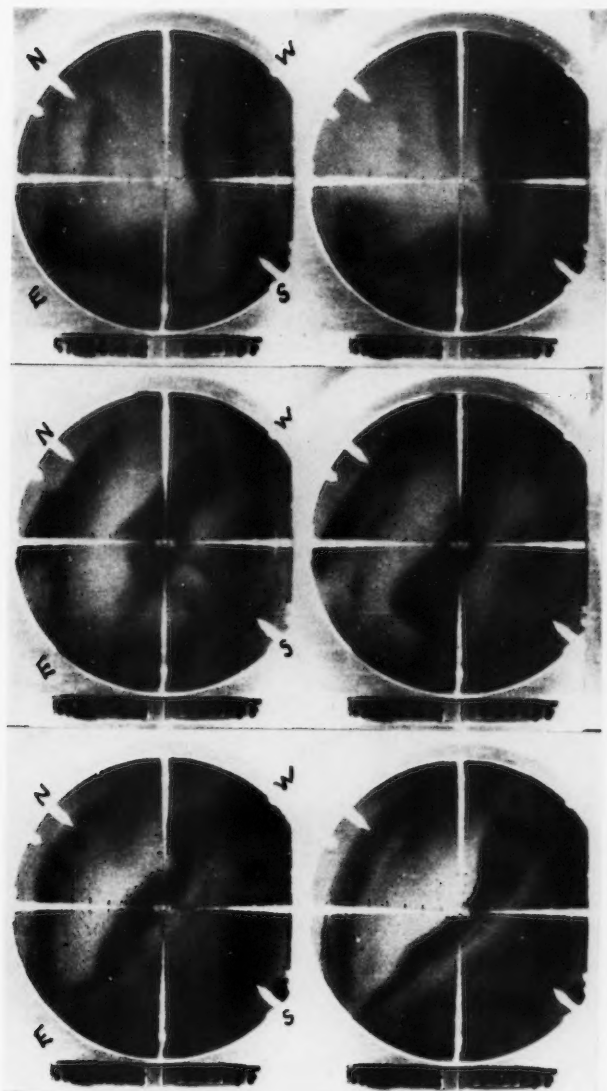
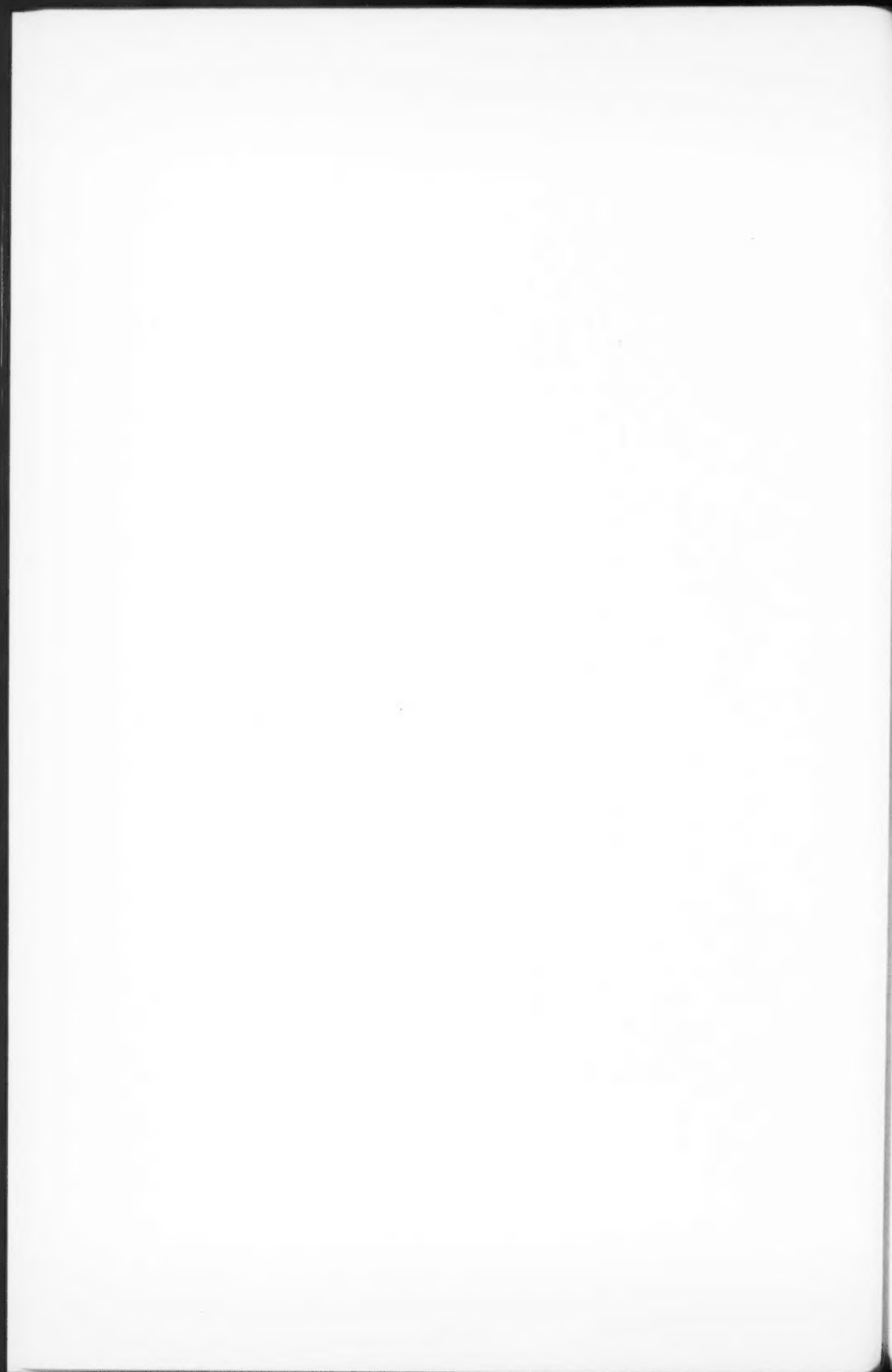


FIG. 1. Some Flin Flon all-sky camera records, showing arcs with "curl" structures, for the night of March 18/19, 1958.
Note that prints are taken from positive film so that the auroral form appears dark.



Thus it is seen that while 14% of all visible aurora could be associated with an echo, only 5% of the quiet arcs could be associated with echoes, the figures for "curls" and active rayed structures being 31% and 14% respectively. Further, it may be noted that

- (a) quiet arcs occurred 40% of the time but accounted for 14% of the echoes;
- (b) "curls" occurred 19% of the time but accounted for 42% of the echoes;
- (c) rayed structures occurred 41% of the time and accounted for 41% of the echoes.

2. Echo and Form Diurnal Variation

Using the same 10-minute periods, the total number of periods in which visible aurora and/or an echo occurred in any one hour throughout the night was computed and plotted against local time as shown in Fig. 2. This diurnal

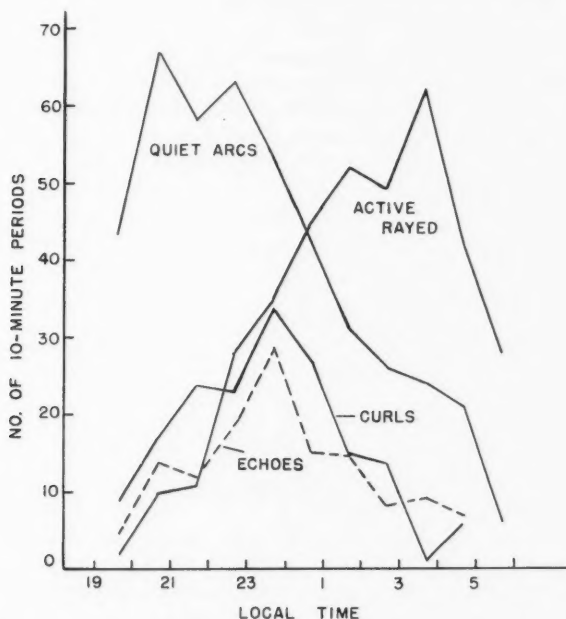


FIG. 2. Diurnal variation of occurrence of visible auroral forms and of echoes.

variation illustrates clearly the general pattern of visible aurora: quiet arcs followed by "curls" and then by active rayed structures. The similarity between the "curl" occurrence curve and the echo occurrence curve is striking.

3. The Direction of the "Curls"

The appearance of an arc developing a "curl" or spiral structure bears a marked resemblance to the characteristic instability profile of a sheet beam of charged particles under the influence of a longitudinal magnetic field.

This fact has also been noted by Gartlein (1959), who has examined qualitatively the expected appearance of an auroral arc assuming the causative agent to be a beam of protons moving downward along the lines of force of the earth's magnetic field. He states that if the beam is not quite uniform, the more intense parts will curve into an S shape figure and if the intensity is raised these curves will go into spirals which, when viewed from the ground looking upward, spiral inward in a clockwise direction. These spirals finally break up into narrow rays. Further, this pattern is not solely an intensity effect but will also occur in a weak beam after more extended travel. Gartlein notes that in the southern hemisphere the spirals observed spiral inward in an anticlockwise direction as would be expected. He concludes that aurora, from the time of arc formation until well after the time of ray formation, is the expected effect of a sheet of protons moving along a magnetic field.

All the spiral forms examined in this investigation spiraled inward in a clockwise direction when viewed from the ground, thus indicating that the primary causative agents for such forms are positively charged particles. Examination of the records of some of the visual observations of aurora made at Chesterfield, N.W.T., during the 1932-33 I.G.Y. (made available by Dr. B. W. Currie, Institute of Upper Atmospheric Physics, University of Saskatchewan) again reveal that when such forms were observed they spiraled in the same direction. Further, Hector (1959), who has examined many all-sky camera records taken from Canadian stations during the 1957-58 I.G.Y. reports over 100 cases of such forms all without exception spiraling in the same direction.

SUMMARY AND DISCUSSION

While the results reported here have been obtained for one station and one frequency (48.2 Mc/sec) only, it would appear that

- (a) the probability of an echo from a quiet arc is small;
- (b) the most probable form which will give an echo is a "curl";
- (c) as active rayed forms occur more frequently than "curls" there is an equal probability of any one echo coming from either a "curl" or an active rayed form.

There is a remarkable similarity between the diurnal variation of echoes and that of "curls" (Fig. 2). The "curl" or spiral form is the one most often seen during the period of breakup of quiet arcs and the formation of rayed structures and is evidently an intermediate form. Thus, there would seem to be a very real case for associating echoes with the period of breakup of quiet arcs into active rayed structures. In this experiment the receiving antenna was fixed in azimuth in a direction 45° east of geomagnetic north. Forsyth (1959) has suggested that a "curl" or spiral form presents a greater volume of ionization to a pulse of electromagnetic radiation than does a quiet arc. Thus, we might expect to receive more echoes from "curl" forms, but by the same token had the radar antenna been directed along the geomagnetic meridian a greater number of echoes might have been obtained from quiet arcs than was obtained with the antenna directed at 45° to the meridian.

All the available evidence from the direction of the "curls" and spirals points to positively charged incoming particles.

Gartlein (1959) has suggested that as particles entering the northern portion of the auroral zone (in the northern hemisphere) traverse longer paths than those entering the southern portion of the zone, then auroras observed in the northern part should more frequently be composed of rayed structures. Possibly more "curls" should be seen also, though in the longer path travelled by the particles the "curl" structure may have developed before the excitation of the visible aurora takes place. It is interesting to note that Collins and Forsyth (1959), in a bistatic radio investigation of auroral ionization over different paths, report that for type A events (signal enhancements related to auroral ionization) occurrence increases with increasing latitude, at least up to the auroral zone. This is just what might be expected if echoes are predominantly associated with "curls" or rayed structures and the occurrence of such structures increases with increasing latitude also.

Forsyth and Green (1959) report that the peak in the diurnal variation of occurrence of type A events occurs progressively earlier with increasing latitude. It is possible that the average time of breakup of quiet arcs into rayed structures also occurs progressively earlier with increasing latitude. It is hoped to report further on this point in a later paper.

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REFERENCES

- COLLINS, C. and FORSYTH, P. A. 1959. *J. Atmospheric and Terrest. Phys.* **13**, 315.
CURRIE, B. W., FORSYTH, P. A., and VAWTER, F. E. 1953. *J. Geophys. Research*, **58**, 179.
FORSYTH, P. A. 1959. Unpublished.
FORSYTH, P. A. and GREEN, F. 1959. Unpublished.
GARTLEIN, C. W. 1959. *Ann. géophys.* **15**, 1, 31.
HECTOR, F. 1959. Private communication.
HEPPNER, J. P. 1954. Ph.D. Thesis, California Institute of Technology, Pasadena, California.
LITTLE, C. G., RAYTON, W. M., and ROOF, R. B. 1956. *Proc. IRE*, **44**, 992.
LYON, G. F. and KAVADAS, A. 1959. *Can. J. Phys.* **36**, 1661.

INFRARED TEMPERATURE AND LINE STRENGTH MEASUREMENTS ON CARBON MONOXIDE EXCITED IN A RADIO-FREQUENCY DISCHARGE¹

D. R. EATON²

ABSTRACT

Relative line intensities in the $2 \rightarrow 0$ sequence of bands of carbon monoxide observed in emission from a radio-frequency discharge have been measured. An enhancement of the *R* branch lines and a diminution of the *P* branch lines due to vibration-rotation interaction has been observed in agreement with theoretical predictions. Vibrational and rotational temperatures have been calculated and when allowance is made for the vibration-rotation interaction these prove to be equal within experimental error indicating the existence of thermal equilibrium in the discharge.

A. INTRODUCTION

The problem of the relative strengths of individual lines in a vibration-rotation band has been the subject of a number of recent papers. The theory of the effect of the interaction of vibration and rotation on the line strengths has been developed by Herman and Wallis (1955) and extended by other authors. The predicted effect has been observed by means of absorption experiments on the fundamental bands of HCl, DCl (Benedict, Herman, Moore, and Silverman 1956, 1957), HF (Kuipers 1958), and DCN (Eaton 1959). In the case of CO the effect on the fundamental is predicted to be too small for observation and this also is in agreement with experiment (Herman, Silverman, and Wallis 1954; Eaton and Thompson 1959).

The results referred to above have all been obtained from absorption spectra but there are some advantages to be gained by carrying out measurements in emission rather than in absorption. In particular the effect of the finite slit width is such that the relative line strengths can be obtained more easily and directly from the actual measurements and the elevated temperature of the gas allows the extension of the measurements to higher *J* values and to vibrationally excited states. In most molecules the discrepancy between *R* and *P* line strengths becomes pronounced only at high *J* values. This type of measurement also provides a method of probing the closely related problem of the existence or otherwise of thermal equilibrium among the various rotational and vibrational energy levels of a gas in a flame or discharge.

The present measurements have been carried out on the $2 \rightarrow 0$ sequence of bands of carbon monoxide. This molecule has a very small dipole moment (μ) so that the parameter $\theta = \mu/(d\mu/dr)$ is also small and the nature of the vibration-rotation interaction is rather different from that in molecules such as HCl and HF for which $\theta \sim 1$. The theoretical treatment of Herman and

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Wallis (1955) and of Herman, Rothery, and Rubin (1958) predicts that the interaction effect in the $2 \rightarrow 0$ band will become appreciable at high J values and that it will be in the opposite sense to that observed in more polar diatomic molecules. This prediction has now been experimentally verified. The intensity distribution in these bands is also of some astrophysical interest since they have been observed in the sun and used to determine solar temperatures (Goldberg and Müller 1953).

B. EXPERIMENTAL

The $2 \rightarrow 0$ sequence of carbon monoxide has been previously observed in emission from flames by Plyler, Benedict, and Silverman (1952) and under lower resolution from an R.F. discharge by Wilkinson, Ford, and Price (1955). The discharge tube used for the present work was of pyrex, 1 meter long and around 10 cm in diameter. It was equipped with a system of multireflection mirrors of the type first suggested by White (1942) for use in absorption work and later adapted for emission experiments by Welsh, Cumming, and Stansburg (1951). It was found that the optimum signal was obtained with a path length of about 40 meters. Power was provided by a 5-kw oscillator operating at 11 Mc/sec. The output from this oscillator could be controlled by adjusting the position of a coupling coil. Power was transferred to the discharge tube either by placing the latter inside a tuned coil or by means of aluminum foil electrodes. The tube was air-cooled but still tended to overheat and crack when the foil electrodes were in use. For this reason the coil method of coupling was used in spite of the rather greater efficiency of the electrodes. Cylinder carbon monoxide was streamed through the tube at a constant pressure of 3 to 4 mm of mercury. Under these conditions a stable discharge giving reproducible line intensities could be maintained for periods of up to 1 hour. The vacuum infrared spectrometer has been described previously (Douglas and Sharma 1953). The detector was a lead sulphide cell cooled to dry ice-acetone temperature and the slit widths employed corresponded to a resolution of about 0.2 cm^{-1} . The amplifier time constant was 0.3 second and the scanning speed was sufficiently slow to allow a maximum throw on the strongest lines. Readjustment of the fore-prism was made every 20 to 30 cm^{-1} .

The variation in the sensitivity of the instrument over the frequency range 3850 cm^{-1} to 4400 cm^{-1} was obtained by calibration with a tungsten filament bulb using the tungsten emissivity curves of De Vos (1954) and the black-body radiation tables of Lowan and Blanch (1940). The temperature of the filament was measured with an optical pyrometer and it was verified by calculation that the *relative* corrections applied are insensitive to possible errors in this temperature.

C. RESULTS

The observed spectrum consisted of the sequence containing the $2 \rightarrow 0$, $3 \rightarrow 1$, $4 \rightarrow 2$, $5 \rightarrow 3$, $6 \rightarrow 4$, and $7 \rightarrow 5$ bands of CO. In addition some lines of the $8 \rightarrow 6$ and $9 \rightarrow 7$ bands were also observed but not in sufficient number

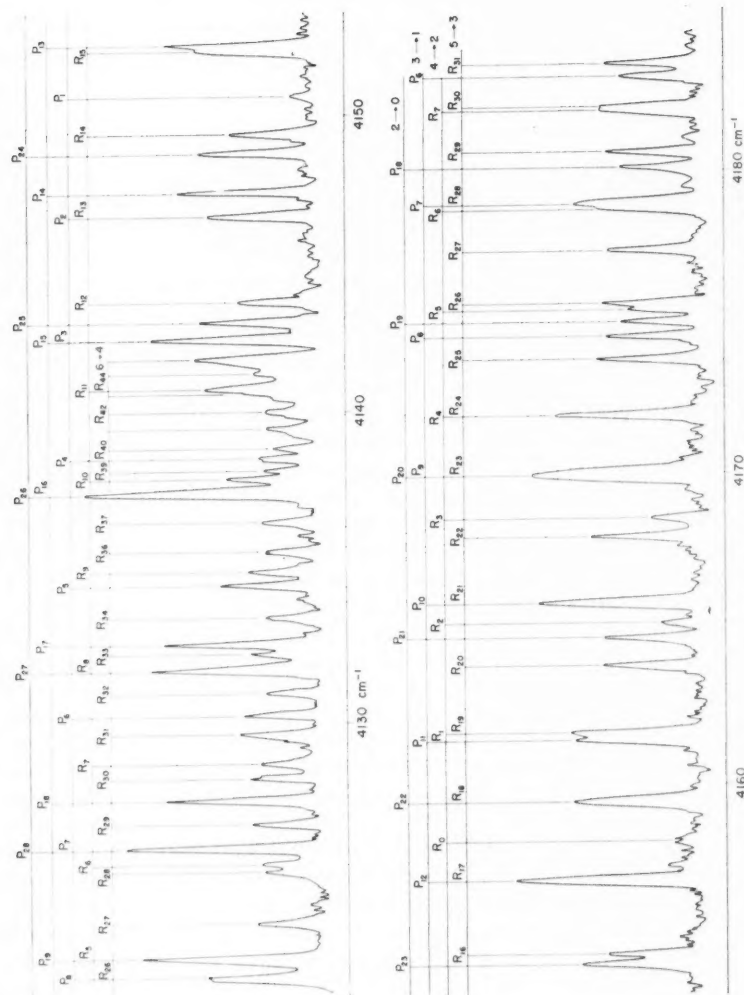


FIG. 1. Radio-frequency discharge spectrum of CO from 4120 cm⁻¹ to 4180 cm⁻¹.

TABLE I
Measured line intensities (peak heights)

Line	2 → 0	3 → 1	4 → 2	5 → 3	6 → 4	7 → 5
P ₁		19.3	11.6			
P ₂		21.0				
P ₃						
P ₄			28.6			
P ₅						
P ₆		43.1	41.3		12.0	
P ₇				25.7		
P ₈		50.5				
P ₉	25.7					15.7
P ₁₀	28.3		47.3	28.7	20.1	
P ₁₁	32.6	66.6		34.2		
P ₁₂	35.2		53.7	31.7	25.5	
P ₁₃	36.8	78.3	50.8	37.1		
P ₁₄		72.7		40.1	23.2	
P ₁₅		85.5	54.5	42.5	22.3	
P ₁₆	45.1	81.6				10.3
P ₁₇		80.3	57.2			
P ₁₈	43.0		61.9		20.5	10.2
P ₁₉	43.0			39.7	21.6	10.1
P ₂₀				41.0	24.9	
P ₂₁	50.7		61.6		28.9	
P ₂₂		78.1		37.9		12.2
P ₂₃	62.7	78.9	63.9	40.7	25.6	
P ₂₄	61.4	74.3		41.5		
P ₂₅	60.9	76.9			23.0	12.0
P ₂₆						
P ₂₇			63.3			
P ₂₈		77.2	61.9			10.3
P ₂₉		74.9	57.3	38.2		13.5
P ₃₀		72.7	56.7	39.1		
P ₃₁		71.9	55.5	39.9		
P ₃₂	62.0	73.1	54.2			
P ₃₃	59.8	67.4	51.7	27.7		
P ₃₄				31.0		
P ₃₅				27.4		
P ₃₆	55.5	69.8				
P ₃₇		65.0	40.8	25.9	17.3	
P ₃₈	48.5	57.0		26.3	16.2	
P ₃₉		57.1	34.7	22.8		
P ₄₀		51.9	35.7		13.4	
P ₄₁	46.0	51.2		19.3	10.1	
P ₄₂	45.5	45.5	36.2			
P ₄₃			33.1	14.7		
P ₄₄						
P ₄₅	36.4	37.2			16.8	
P ₄₆	34.6	37.4	34.7		16.1	
P ₄₇	35.5	33.5				
P ₄₈	30.6	25.6			15.5	
P ₄₉	27.6		27.5			
P ₅₀	24.8	23.0		9.5		
P ₅₁		29.6	18.5			
P ₅₂	22.3		12.4			
P ₅₃	19.0	21.9	8.1			
P ₅₄		15.0				
P ₅₅	16.9	16.6				
P ₅₆		13.2				
P ₅₇						
P ₅₈		15.2				
P ₅₉		14.1				

or with sufficient intensity for the present type of measurement. A portion of the spectrum is shown in Fig. 1 to indicate the degree of resolution. About 50 to 60% of the total number of lines was sufficiently free from overlap to allow reliable measurement. The measured relative intensities of these lines, corrected for changes in instrumental sensitivity, are given in Table I. The absolute values are arbitrary.

The amount of light emerging from the exit slit of the spectrometer when it is set on the center of an emission line is given by an expression of the type

$$(1) \quad T_{\nu'} = \text{constant } I_m \int_0^{\infty} f_1(\gamma, \nu - \nu') f_2(a, \nu - \nu') d\nu \dots$$

I_m is the integrated intensity of the m th line and f_1 and f_2 are functions describing the line shape and spectrometer slit function respectively. They involve γ , the line width parameter (f_1), and a , the spectral slit width (f_2). Equation (1) is much simpler than the corresponding expression for absorption in that $T_{\nu'}$ is directly proportional to I_m . Under the present experimental conditions the line width arising from Doppler broadening will be around 0.01 cm^{-1} and that from pressure broadening $< 0.001 \text{ cm}^{-1}$ (Eaton and Thompson 1959). Natural line width is negligible in the infrared. Since the slit width a is $\sim 0.2 \text{ cm}^{-1}$ the slit function f_2 will therefore be approximately constant over the range of frequencies for which f_1 is appreciably large and can therefore be removed from the integral in equation (1). Variation of slit width with frequency is therefore absorbed into the instrumental sensitivity correction. Further, when f_2 has been removed the remaining integral $\int f_1 d\nu$ must by the definition of integrated line intensity be a constant independent of the line width γ . The values given in Table I will therefore be used as a direct measure of the line intensities.

There is a source of error in emission intensity measurements which should also be considered, namely that arising from self-absorption. Errors from this source will be greatest in lines arising from transitions to heavily populated lower states, i.e. to the lower-lying vibrational energy levels and J values. Fortunately it is the high J values which are most significant in the present case. Preliminary experiments showed that self-absorption from gas in the cooler parts of the tube was appreciable for the $2 \rightarrow 0$ band and revealed itself as a distinct curvature in the temperature plot. The measurements from this band have not therefore been used in any of the subsequent calculations. There is, however, no indication of a significant effect in the higher bands and the results from these latter are thought to be reliable.

D. DISCUSSION

The intensity of an emission line in a vibration-rotation band is given by an expression of the type

$$(2) \quad I_m = \text{constant } \nu^4 F(m) (J' + J'' + 1) \exp\left(-\frac{hc}{kT} E_J'\right).$$

The function $F(m)$ (where $m = -J$ for the P branch and $m = J+1$ for the R branch) is introduced to allow for the vibration-rotation interaction. The

other symbols have their usual significance. $F(m)$ is unity at the band origin but becomes increasingly different from unity at higher J values. If $F(m)$ were unity at all J values, i.e. no vibration-rotation interaction, the rotational temperature could be found by plotting $\log \{I/[v^4(J'+J''+1)]\}$ against E'_J and obtaining the slope. If, however, the F values for the corresponding lines in the P and R branches are not equal the points for the two branches will fall on separate curves. The separation of the curves will give the ratio of the F factors at a given value of m but the method of temperature determination will fail. Figure 2 shows this plot for the $3 \rightarrow 1$ band. The results for the other bands are very similar. The frequencies and energy levels were calcu-

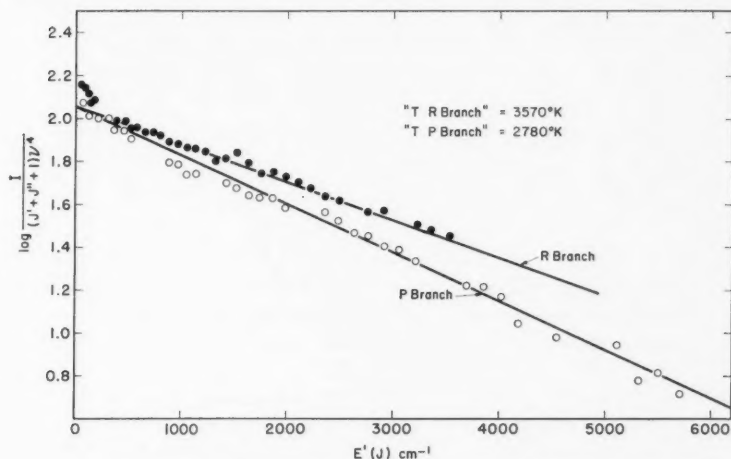


FIG. 2. "Rotational temperature" plot for the $3 \rightarrow 1$ band.

lated from the molecular constants given by Plyler, Benedict, and Silverman (1952). It is apparent that the F factors are appreciably different in the two branches, being largest in the R branch which is in accord with the theoretical treatment of Herman, Rothery, and Rubin (1958). Straight lines drawn through the points for the two branches gave approximate apparent temperatures of 3570°K and 2780°K and since the theory predicts that $F(m)$ will be greater than unity and $F(-m)$ less than unity by roughly equal amounts the true temperature will be between these values and may be estimated as around 3175°K . It is not possible, however, to obtain either the temperature or the F factors independently from these plots.

A vibrational temperature may be obtained from the relative intensities of corresponding lines in the different bands of the sequence. As many pairs as possible from both P and R branches were chosen and from the average ratios the intensities of the other bands relative to the $3 \rightarrow 1$ band were calculated. It is also necessary to know the vibrational transition probabilities (M^2) and the values given by Herman (1952) were taken. These are stated to be uncertain to the extent of 10%. Figure 3 shows the plot of $\log (I/M^2v^4)$

against E' (vib.). This leads to a vibrational temperature of 3120°K . Bearing in mind the approximations involved in both cases this value is probably sufficiently close to the estimated rotational temperature of 3175°K to indicate the existence of thermal equilibrium between the vibrational and rotational energies. It is interesting to note that from the flame spectrum of

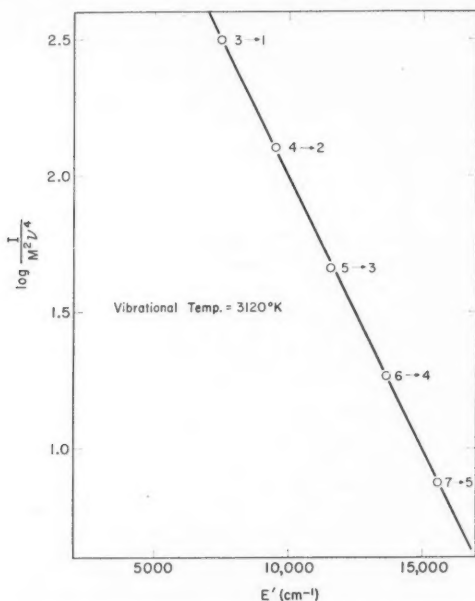


FIG. 3. Vibrational temperature plot for the $2 \rightarrow 0$ sequence of bands.

CO Plyler, Benedict, and Silverman obtained a vibrational temperature of 2360°K and a rotational temperature of 2800°K . This latter temperature, though, was obtained only from R branch lines and the apparent discrepancy is very similar to the corresponding quantity obtained from the present discharge spectrum (3570°K rotational, 3120°K vibrational). A correct allowance for the vibration-rotation interaction could well produce agreement between the two temperatures. It would seem from this that the conditions of energy transfer in carbon monoxide flames and discharges are quite similar and that in both cases there is a sufficiently close approximation to thermal equilibrium to give a physical meaning to the temperature values obtained.

In order to further substantiate this conclusion the vibrational value of 3120°K was taken as a rotational temperature and used to obtain the F values from equation (2). The results are illustrated in Fig. 4, points from the $3 \rightarrow 1$ and $4 \rightarrow 2$ bands being included. The solid curves are obtained from the theory of Herman, Rothery, and Rubin. The theoretically calculated

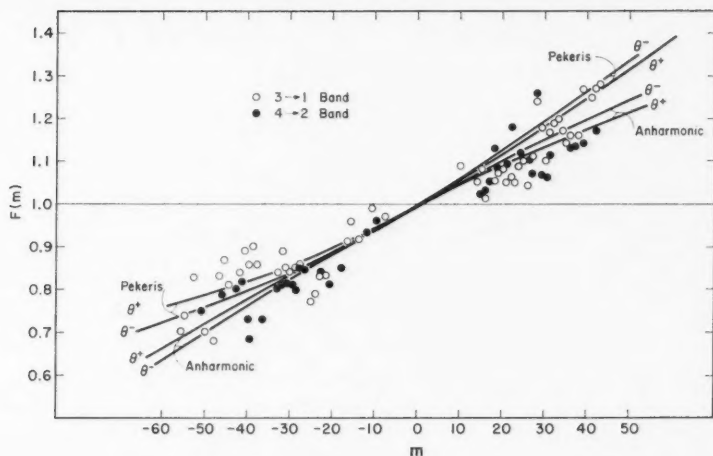


FIG. 4. Comparison of experimental and theoretical F values.

values depend on the form of the potential field assumed and curves for both an anharmonic oscillator and for a Pekeris oscillator are included. The F values also depend on whether the signs of the dipole moment μ and its derivative $d\mu/dr$ for CO are the same or opposite and the curves labelled θ^+ and θ^- represent these alternatives. As can be seen from Fig. 4 the experimental F factors agree well with the theoretical values within the experimental error but this error is too large to enable a choice to be made between the different types of oscillator or between the alternative signs of θ . The F factors for the higher bands show no systematic deviation from those for the lower bands. This also would seem to be in agreement with theoretical expectations.

It may be concluded that the Herman and Wallis theory gives a satisfactory account of the effects of vibration-rotation interaction for the present case where θ is small and the anharmonic effects are predominant as well as for cases previously studied where θ is large. An allowance for this effect must be made if meaningful temperatures are to be obtained from intensity measurements and in the present case the results show that thermal equilibrium between the vibrational and rotational energies has been attained. The results obtained also indicate that in some cases infrared intensities can with profit be studied in emission rather than in absorption. This may prove to be particularly true in the case of unstable radicals such as OH.

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REFERENCES

- BENEDICT, W. S., HERMAN, R., MOORE, G. E., and SILVERMAN, S. 1956. *Can. J. Phys.* **34**, 830.
- BENEDICT, W. S., HERMAN, R., MOORE, G. E., and SILVERMAN, S. 1957. *J. Chem. Phys.* **26**, 1671.
- DE VOS, J. C. 1954. *Physica*, **20**, 690.
- DOUGLAS, A. E. and SHARMA, D. 1953. *J. Chem. Phys.* **21**, 448.
- EATON, D. R. 1959. *Proc. Roy. Soc. A*, **251**, 486.
- EATON, D. R. and THOMPSON, H. W. 1959. *Proc. Roy. Soc. A*, **251**, 458.
- GOLDBERG, L. and MÜLLER, E. A. 1953. *Astrophys. J.* **118**, 397.
- HERMAN, R. 1952. *Quoted in* Plyler, Benedict, and Silverman (1952).
- HERMAN, R. and WALLIS, R. F. 1955. *J. Chem. Phys.* **23**, 637.
- HERMAN, R., SILVERMAN, S., and WALLIS, R. F. 1954. *Phys. Rev.* **94**, 752.
- HERMAN, R., ROTHERY, R. W., and RUBIN, R. J. 1958. *J. Molecular Spectroscopy*, **2**, 369.
- KUIPERS, G. A. 1958. *J. Molecular Spectroscopy*, **2**, 75.
- LOWAN, A. N. and BLANCH, G. 1940. *J. Opt. Soc. Am.* **30**, 70.
- PLYLER, E. K., BENEDICT, W. S., and SILVERMAN, S. 1952. *J. Chem. Phys.* **20**, 175.
- WILKINSON, G. R., FORD, M. A., and PRICE, W. C. 1955. *Molecular Spectroscopy*, Institute of Petroleum.
- WELSH, H. L., CUMMING, C., and STANSBURG, E. J. 1951. *J. Opt. Soc. Am.* **41**, 712.
- WHITE, J. U. 1942. *J. Opt. Soc. Am.* **32**, 285.

TABLES OF THE MODIFIED BESSEL FUNCTIONS OF THE SECOND KIND FOR PARTICULAR TYPES OF ARGUMENT¹

E. DEMPSEY² AND G. C. BENSON

ABSTRACT

Tables of the modified Bessel functions of the second kind $K_n(z)$ for arguments z of the form $(\pi/2)\sqrt{q}$ and $(\pi/3)\sqrt{q}$ where q is an integer and for all integral and half-integral orders n in the range 0–10.5 are presented. For all but a small range of the argument the tables can be relied upon to the 10 figures given; in the omitted range an error of unity in the 10th place may occur. The tables should be useful for the computation of many lattice sums arising in the theoretical calculation of crystal properties.

1. INTRODUCTION

For the theoretical calculation of the properties of ionic crystals it is important to be able to evaluate, reasonably accurately, various summations over the lattice sites, where the quantities summed are usually potential functions involving inverse powers of the distances from the ions to the point at which the potential is required. Since these functions may represent the relatively long-range attractive interactions arising from the electrostatic and dispersive forces within the crystal, it is not surprising that often their sums do not converge very rapidly. Occasionally for inverse powers greater than about three or four, summations of this type have been carried out by direct addition of terms for a large number of lattice points, the summation being completed by an integration over the remainder of the lattice (Lennard-Jones and Dent 1928; Shuttleworth 1949). Alternatively the summation may be effected by transforming the sum to a more rapidly converging form and summing the resulting series directly (see, for instance, Madelung 1918; and van der Hoff and Benson 1953). The latter approach has been used fairly recently in papers dealing with the Coulomb and van der Waals potentials associated with the problem of the adsorption of polarizable atoms or ions onto the surface of an infinite hemicrystal (Hove and Krumhansl 1953; Hartman 1956; Durham and Soderberg 1958) and for the calculation of edge energies (Schreiber and Benson 1955) and surface energies (van Zeggeren and Benson 1957; Benson, Balk, and White 1959; Benson, Dempsey, and Balk, unpublished). All of these applications have the common ground that the series resulting from the various transformations involve the modified Bessel functions of the second kind, $K_n(z)$, although frequently other transcendental functions also arise. For the definition of $K_n(z)$ used here see Watson (1948).

In the work originating from this laboratory (references above to Benson and co-workers) it has been found that the arguments of the Bessel functions

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which have occurred so far have integral and half-integral orders n in the range 0-8 and that the arguments may all be expressed in one or other of the general forms:

$$(1) \quad \begin{cases} z = \frac{\pi}{2} \sqrt{q} \\ z = \frac{\pi}{3} \sqrt{q} \end{cases}$$

where q is an integer.

In problems involving distortion of the lattice surface, the potential energies required usually have to be evaluated at points off the regular lattice array. Since the displacements from the regular sites are, in general, small, the summations required may, in these cases, be expanded in Taylor series about a zero displacement. This allows the original summation to be expressed as a linear combination of a number of summations involving functions of the form (1), but with orders which, in general, are higher than those of the original summation. For problems concerned with the interaction of ions situated at an arbitrary distance z above an infinite hemicrystal (as in the references to adsorption problems given above) the argument of the Bessel functions will usually include z . In many of these cases it should also be possible to remove the variable z from the argument by a suitable series expansion.

In order to facilitate the evaluation of lattice summations in our own work, tables of the modified Bessel functions for arguments of the forms (1) have been computed for a fairly wide range of orders and arguments. The purpose of this paper is to present these in the hope that they may be of use to other workers.

2. CALCULATION OF THE TABLES

The computation of the tables was carried out entirely on a Bendix G 15D digital computer operating in a double-precision floating point mode. Although this gave 12 figures in the final results, the entries in the tables were eventually rounded off to 10 figures. To simplify the presentation, the tables have been left in the floating point notation, in which the two figures to the left of the point indicate, on an excess 50 basis, the power of 10 by which the remaining decimal part must be multiplied. This notation should be evident from the following examples:

$$\begin{aligned} 46.123 &\equiv 0.123 \times 10^{-4} \\ 50.123 &\equiv 0.123 \\ 55.123 &\equiv 0.123 \times 10^5 \end{aligned}$$

The basis for most of the computation was the asymptotic expansion for $K_n(z)$:

$$(2) \quad K_n(z) = \left(\frac{\pi}{2z}\right)^{\frac{1}{2}} e^{-z} \left[1 + \frac{4n^2 - 1^2}{(8z)1!} + \frac{(4n^2 - 1^2)(4n^2 - 3^2)}{(8z)^2 2!} + \dots \right].$$

$K_n(\frac{x}{\sqrt{q}})$

q	n	1	2	3	4	5	6	7	8	9	10
1	1	50.19312071271	50.202732596	50.313665479	51.647729405	52.348506926	53.282666274	54.176877434	55.1594723913	56.16001214	57.1897513488
2	1	49.8697010871	50.104975064	50.431768380	51.327729405	52.348506926	53.282666274	54.176877434	55.1594723913	56.16001214	57.1897513488
3	1	49.4807569266	49.895822665	49.895822665	50.505377283	51.647729405	52.348506926	53.282666274	54.176877434	55.1594723913	56.16001214
4	1	49.2407569266	49.391303099	49.104969266	49.9897477621	50.716047680	51.716047680	52.485662921	53.3094354262	54.1006367158	54.6823926151
5	1	49.0407569266	49.140409128	49.140409128	49.311292791	50.319767694	51.4627593323	51.807771053	52.875421238	53.4646766673	54.1464676673
6	1	48.8407569266	48.940409128	48.940409128	49.111292791	50.119767694	51.2627593323	51.607771053	52.675421238	53.2646766673	53.9464676673
7	1	48.6407569266	48.740409128	48.740409128	48.941311995	49.141311995	49.341311995	49.541311995	49.741311995	49.941311995	50.141311995
8	1	48.4407569266	48.540409128	48.540409128	48.741311995	48.941311995	49.141311995	49.341311995	49.541311995	49.741311995	49.941311995
9	1	48.2407569266	48.340409128	48.340409128	48.541311995	48.741311995	48.941311995	49.141311995	49.341311995	49.541311995	49.741311995
10	1	48.0407569266	48.140409128	48.140409128	47.941311995	48.141311995	48.341311995	48.541311995	48.741311995	48.941311995	49.141311995
11	1	47.8407569266	47.940409128	47.940409128	47.741311995	47.941311995	48.141311995	48.341311995	48.541311995	48.741311995	48.941311995
12	1	47.6407569266	47.740409128	47.740409128	47.541311995	47.741311995	47.941311995	48.141311995	48.341311995	48.541311995	48.741311995
13	1	47.4407569266	47.540409128	47.540409128	47.341311995	47.541311995	47.741311995	47.941311995	48.141311995	48.341311995	48.541311995
14	1	47.2407569266	47.340409128	47.340409128	47.141311995	47.341311995	47.541311995	47.741311995	47.941311995	48.141311995	48.341311995
15	1	47.0407569266	47.140409128	47.140409128	46.941311995	47.141311995	47.341311995	47.541311995	47.741311995	47.941311995	48.141311995
16	1	46.8407569266	46.940409128	46.940409128	46.741311995	46.941311995	47.141311995	47.341311995	47.541311995	47.741311995	47.941311995
17	1	46.6407569266	46.740409128	46.740409128	46.541311995	46.741311995	46.941311995	47.141311995	47.341311995	47.541311995	47.741311995
18	1	46.4407569266	46.540409128	46.540409128	46.341311995	46.541311995	46.741311995	46.941311995	47.141311995	47.341311995	47.541311995
19	1	46.2407569266	46.340409128	46.340409128	46.141311995	46.341311995	46.541311995	46.741311995	46.941311995	47.141311995	47.341311995
20	1	46.0407569266	46.140409128	46.140409128	45.941311995	46.141311995	46.341311995	46.541311995	46.741311995	46.941311995	47.141311995
21	1	45.8407569266	45.940409128	45.940409128	45.741311995	45.941311995	46.141311995	46.341311995	46.541311995	46.741311995	46.941311995
22	1	45.6407569266	45.740409128	45.740409128	45.541311995	45.741311995	45.941311995	46.141311995	46.341311995	46.541311995	46.741311995
23	1	45.4407569266	45.540409128	45.540409128	45.341311995	45.541311995	45.741311995	45.941311995	46.141311995	46.341311995	46.541311995
24	1	45.2407569266	45.340409128	45.340409128	45.141311995	45.341311995	45.541311995	45.741311995	45.941311995	46.141311995	46.341311995
25	1	45.0407569266	45.140409128	45.140409128	44.941311995	45.141311995	45.341311995	45.541311995	45.741311995	45.941311995	46.141311995
26	1	44.8407569266	44.940409128	44.940409128	44.741311995	44.941311995	45.141311995	45.341311995	45.541311995	45.741311995	45.941311995
27	1	44.6407569266	44.740409128	44.740409128	44.541311995	44.741311995	44.941311995	45.141311995	45.341311995	45.541311995	45.741311995
28	1	44.4407569266	44.540409128	44.540409128	44.341311995	44.541311995	44.741311995	44.941311995	45.141311995	45.341311995	45.541311995
29	1	44.2407569266	44.340409128	44.340409128	44.141311995	44.341311995	44.541311995	44.741311995	44.941311995	45.141311995	45.341311995
30	1	44.0407569266	44.140409128	44.140409128	43.941311995	44.141311995	44.341311995	44.541311995	44.741311995	44.941311995	45.141311995
31	1	43.8407569266	43.940409128	43.940409128	43.741311995	43.941311995	44.141311995	44.341311995	44.541311995	44.741311995	44.941311995
32	1	43.6407569266	43.740409128	43.740409128	43.541311995	43.741311995	43.941311995	44.141311995	44.341311995	44.541311995	44.741311995
33	1	43.4407569266	43.540409128	43.540409128	43.341311995	43.541311995	43.741311995	43.941311995	44.141311995	44.341311995	44.541311995
34	1	43.2407569266	43.340409128	43.340409128	43.141311995	43.341311995	43.541311995	43.741311995	43.941311995	44.141311995	44.341311995
35	1	43.0407569266	43.140409128	43.140409128	42.941311995	43.141311995	43.341311995	43.541311995	43.741311995	43.941311995	44.141311995
36	1	42.8407569266	42.940409128	42.940409128	42.741311995	42.941311995	43.141311995	43.341311995	43.541311995	43.741311995	43.941311995
37	1	42.6407569266	42.740409128	42.740409128	42.541311995	42.741311995	42.941311995	43.141311995	43.341311995	43.541311995	43.741311995
38	1	42.4407569266	42.540409128	42.540409128	42.341311995	42.541311995	42.741311995	42.941311995	43.141311995	43.341311995	43.541311995
39	1	42.2407569266	42.340409128	42.340409128	42.141311995	42.341311995	42.541311995	42.741311995	42.941311995	43.141311995	43.341311995
40	1	42.0407569266	42.140409128	42.140409128	41.941311995	42.141311995	42.341311995	42.541311995	42.741311995	42.941311995	43.141311995
41	1	41.8407569266	41.940409128	41.940409128	41.741311995	41.941311995	42.141311995	42.341311995	42.541311995	42.741311995	42.941311995
42	1	41.6407569266	41.740409128	41.740409128	41.541311995	41.741311995	41.941311995	42.141311995	42.341311995	42.541311995	42.741311995
43	1	41.4407569266	41.540409128	41.540409128	41.341311995	41.541311995	41.741311995	41.941311995	42.141311995	42.341311995	42.541311995
44	1	41.2407569266	41.340409128	41.340409128	41.141311995	41.341311995	41.541311995	41.741311995	41.941311995	42.141311995	42.341311995
45	1	41.0407569266	41.140409128	41.140409128	40.941311995	41.141311995	41.341311995	41.541311995	41.741311995	41.941311995	42.141311995
46	1	40.8407569266	40.940409128	40.940409128	40.741311995	40.941311995	41.141311995	41.341311995	41.541311995	41.741311995	41.941311995
47	1	40.6407569266	40.740409128	40.740409128	40.541311995	40.741311995	40.941311995	41.141311995	41.341311995	41.541311995	41.741311995
48	1	40.4407569266	40.540409128	40.540409128	40.341311995	40.541311995	40.741311995	40.941311995	41.141311995	41.341311995	41.541311995
49	1	40.2407569266	40.340409128	40.340409128	40.141311995	40.341311995	40.541311995	40.741311995	40.941311995	41.141311995	41.341311995
50	1	40.0407569266	40.140409128	40.140409128	39.941311995	40.141311995	40.341311995	40.541311995	40.741311995	40.941311995	41.141311995

$K_n \left(\frac{z}{\sqrt{q}} \right)$

q	0	1	2	3	4	5	6	7	8	9	10
51	45.1471568001	45.1500694883	45.5989013847	45.7294160173	45.9800423849	46.1468339919	46.2823330216	46.3888066601	46.7044345118	47.1386613249	47.2593576326
52	45.1473558001	45.1502684883	45.5990913847	45.7306160173	45.9812423849	46.1480339919	46.2835330216	46.3900066601	46.7156345118	47.1508613249	47.2715576326
53	45.1475558001	45.1504684883	45.5992813847	45.7318160173	45.9824423849	46.1492339919	46.2847330216	46.3912066601	46.7368345118	47.1720613249	47.2927576326
54	45.1477558001	45.1506684883	45.5994713847	45.7330160173	45.9836423849	46.1504339919	46.2859330216	46.3924066601	46.7580345118	47.1932613249	47.3139576326
55	45.1479558001	45.1508684883	45.5996613847	45.7342160173	45.9848423849	46.1516339919	46.2871330216	46.3936066601	46.7792345118	47.2144613249	47.3351576326
56	45.1481558001	45.1510684883	45.5998513847	45.7354160173	45.9860423849	46.1528339919	46.2883330216	46.3948066601	46.8004345118	47.2356613249	47.3563576326
57	45.1483558001	45.1512684883	45.6000413847	45.7366160173	45.9872423849	46.1540339919	46.2895330216	46.3960066601	46.8216345118	47.2568613249	47.3775576326
58	45.1485558001	45.1514684883	45.6002313847	45.7378160173	45.9884423849	46.1552339919	46.2907330216	46.3972066601	46.8428345118	47.2780613249	47.3987576326
59	45.1487558001	45.1516684883	45.6004213847	45.7390160173	45.9896423849	46.1564339919	46.2919330216	46.3984066601	46.8640345118	47.2992613249	47.4199576326
60	45.1489558001	45.1518684883	45.6006113847	45.7402160173	45.9908423849	46.1576339919	46.2931330216	46.3996066601	46.8852345118	47.3204613249	47.4411576326
61	45.1491558001	45.1520684883	45.6008013847	45.7414160173	45.9920423849	46.1588339919	46.2943330216	46.4008066601	46.9064345118	47.3416613249	47.4623576326
62	45.1493558001	45.1522684883	45.6010013847	45.7426160173	45.9932423849	46.1600339919	46.2955330216	46.4020066601	46.9276345118	47.3628613249	47.4835576326
63	45.1495558001	45.1524684883	45.6011913847	45.7438160173	45.9944423849	46.1612339919	46.2967330216	46.4032066601	46.9488345118	47.3840613249	47.5047576326
64	45.1497558001	45.1526684883	45.6013813847	45.7450160173	45.9956423849	46.1624339919	46.2979330216	46.4044066601	46.9700345118	47.4052613249	47.5259576326
65	45.1499558001	45.1528684883	45.6015713847	45.7462160173	45.9968423849	46.1636339919	46.2991330216	46.4056066601	46.9912345118	47.4264613249	47.5471576326
66	45.1501558001	45.1530684883	45.6017613847	45.7474160173	45.9980423849	46.1648339919	46.3003330216	46.4068066601	47.0124345118	47.4476613249	47.5683576326
67	45.1503558001	45.1532684883	45.6019513847	45.7486160173	45.9992423849	46.1660339919	46.3015330216	46.4080066601	47.0336345118	47.4688613249	47.5895576326
68	45.1505558001	45.1534684883	45.6021413847	45.7498160173	46.0004423849	46.1672339919	46.3027330216	46.4092066601	47.0548345118	47.4900613249	47.6107576326
69	45.1507558001	45.1536684883	45.6023313847	45.7510160173	46.0016423849	46.1684339919	46.3039330216	46.4104066601	47.0760345118	47.5112613249	47.6319576326
70	45.1509558001	45.1538684883	45.6025213847	45.7522160173	46.0028423849	46.1696339919	46.3051330216	46.4116066601	47.0972345118	47.5324613249	47.6531576326
71	45.1511558001	45.1540684883	45.6027113847	45.7534160173	46.0040423849	46.1708339919	46.3063330216	46.4128066601	47.1184345118	47.5536613249	47.6743576326
72	45.1513558001	45.1542684883	45.6029013847	45.7546160173	46.0052423849	46.1720339919	46.3075330216	46.4140066601	47.1396345118	47.5748613249	47.6955576326
73	45.1515558001	45.1544684883	45.6030913847	45.7558160173	46.0064423849	46.1732339919	46.3087330216	46.4152066601	47.1608345118	47.5960613249	47.7167576326
74	45.1517558001	45.1546684883	45.6032813847	45.7570160173	46.0076423849	46.1744339919	46.3099330216	46.4164066601	47.1820345118	47.6172613249	47.7379576326
75	45.1519558001	45.1548684883	45.6034713847	45.7582160173	46.0088423849	46.1756339919	46.3111330216	46.4176066601	47.2032345118	47.6384613249	47.7591576326
76	45.1521558001	45.1550684883	45.6036613847	45.7594160173	46.0100423849	46.1768339919	46.3123330216	46.4188066601	47.2244345118	47.6596613249	47.7803576326
77	45.1523558001	45.1552684883	45.6038513847	45.7606160173	46.0112423849	46.1780339919	46.3135330216	46.4200066601	47.2456345118	47.6808613249	47.8015576326
78	45.1525558001	45.1554684883	45.6040413847	45.7618160173	46.0124423849	46.1792339919	46.3147330216	46.4212066601	47.2668345118	47.7020613249	47.8227576326
79	45.1527558001	45.1556684883	45.6042313847	45.7630160173	46.0136423849	46.1804339919	46.3159330216	46.4224066601	47.2880345118	47.7232613249	47.8439576326
80	45.1529558001	45.1558684883	45.6044213847	45.7642160173	46.0148423849	46.1816339919	46.3171330216	46.4236066601	47.3092345118	47.7444613249	47.8651576326
81	45.1531558001	45.1560684883	45.6046113847	45.7654160173	46.0160423849	46.1828339919	46.3183330216	46.4248066601	47.3304345118	47.7656613249	47.8863576326
82	45.1533558001	45.1562684883	45.6048013847	45.7666160173	46.0172423849	46.1840339919	46.3195330216	46.4260066601	47.3516345118	47.7868613249	47.9075576326
83	45.1535558001	45.1564684883	45.6049913847	45.7678160173	46.0184423849	46.1852339919	46.3207330216	46.4272066601	47.3728345118	47.8080613249	47.9287576326
84	45.1537558001	45.1566684883	45.6051813847	45.7690160173	46.0196423849	46.1864339919	46.3219330216	46.4284066601	47.3940345118	47.8292613249	47.9499576326
85	45.1539558001	45.1568684883	45.6053713847	45.7702160173	46.0208423849	46.1876339919	46.3231330216	46.4296066601	47.4152345118	47.8504613249	47.9711576326
86	45.1541558001	45.1570684883	45.6055613847	45.7714160173	46.0220423849	46.1888339919	46.3243330216	46.4308066601	47.4364345118	47.8716613249	47.9923576326
87	45.1543558001	45.1572684883	45.6057513847	45.7726160173	46.0232423849	46.1900339919	46.3255330216	46.4320066601	47.4576345118	47.8928613249	48.0135576326
88	45.1545558001	45.1574684883	45.6059413847	45.7738160173	46.0244423849	46.1912339919	46.3267330216	46.4332066601	47.4788345118	47.9140613249	48.0347576326
89	45.1547558001	45.1576684883	45.6061313847	45.7750160173	46.0256423849	46.1924339919	46.3279330216	46.4344066601	47.5000345118	47.9352613249	48.0559576326
90	45.1549558001	45.1578684883	45.6063213847	45.7762160173	46.0268423849	46.1936339919	46.3291330216	46.4356066601	47.5212345118	47.9564613249	48.0771576326
91	45.1551558001	45.1580684883	45.6065113847	45.7774160173	46.0280423849	46.1948339919	46.3303330216	46.4368066601	47.5424345118	47.9776613249	48.0983576326
92	45.1553558001	45.1582684883	45.6067013847	45.7786160173	46.0292423849	46.1960339919	46.3315330216	46.4380066601	47.5636345118	47.9988613249	48.1195576326
93	45.1555558001	45.1584684883	45.6068913847	45.7798160173	46.0304423849	46.1972339919	46.3327330216	46.4392066601	47.5848345118	48.0200613249	48.1407576326
94	45.1557558001	45.1586684883	45.6070813847	45.7810160173	46.0316423849	46.1984339919	46.3339330216	46.4404066601	47.6060345118	48.0412613249	48.1619576326
95	45.1559558001	45.1588684883	45.6072713847	45.7822160173	46.0328423849	46.1996339919	46.3351330216	46.4416066601	47.6272345118	48.0624613249	48.1831576326
96	45.1561558001	45.1590684883	45.6074613847	45.7834160173	46.0340423849	46.2008339919	46.3363330216	46.4428066601	47.6484345118	48.0836613249	48.2043576326
97	45.1563558001	45.1592684883	45.6076513847	45.7846160173	46.0352423849	46.2020339919	46.3375330216	46.4440066601	47.6696345118	48.1048613249	48.2255576326
98	45.1565558001	45.1594684883	45.6078413847	45.7858160173	46.0364423849	46.2032339919	46.3387330216	46.4452066601	47.6908345118	48.1260613249	48.2467576326
99	45.1567558001	45.1596684883	45.6080313847	45.7870160173	46.0376423849	46.2044339919	46.3399330216	46.4464066601	47.7120345118	48.1472613249	48.2679576326
100	45.1569558001	45.1598684883	45.6082213847	45.7882160173	46.0388423849	46.2056339919	46.3411330216	46.4476066601	47.7332345118	48.1684613249	48.2891576326

$K_n(\sqrt{x})$

q	0	1	2	3	4	5	6	7	8	9	10
121	43.436501362	43.426004001	43.4291772900	43.4378657815	43.451613391	43.469392685	43.491161587	43.516876615	43.546529552	43.58004817	43.61764115
122	43.437552552	43.426955176	43.430128465	43.438816956	43.452564566	43.470343860	43.492112758	43.517827786	43.547480723	43.58100034	43.61859335
123	43.438603742	43.427906366	43.431079655	43.439768146	43.453515756	43.471295050	43.493063948	43.518778976	43.548431913	43.58195153	43.61954454
124	43.439654932	43.428757556	43.431930845	43.440619336	43.454366946	43.472146240	43.493915138	43.519630166	43.549283103	43.58280272	43.62039573
125	43.440706122	43.429808746	43.432982035	43.441670526	43.455418136	43.473197430	43.494966328	43.520681356	43.550334293	43.58385391	43.62144692
126	43.441757312	43.430859936	43.434033225	43.442721716	43.456469326	43.474248620	43.496017518	43.521732546	43.551385483	43.58490510	43.62249791
127	43.442808502	43.431911126	43.435084415	43.443772906	43.457520516	43.475300810	43.497069708	43.522784736	43.552437673	43.58595729	43.62354890
128	43.443859692	43.432962316	43.436135605	43.444824096	43.458571706	43.476352000	43.498120898	43.523835926	43.553488863	43.58700848	43.62459989
129	43.444910882	43.434013506	43.437186795	43.445875286	43.459622896	43.477403190	43.499172088	43.524887116	43.554540053	43.58805967	43.62565088
130	43.445962072	43.435064696	43.438237985	43.446926476	43.460674086	43.478454380	43.500223278	43.525838306	43.555491243	43.58901086	43.62670187
131	43.447013262	43.436115886	43.439289175	43.447977666	43.461725276	43.479505570	43.501274468	43.526889496	43.556542433	43.59006205	43.62775286
132	43.448064452	43.437167076	43.440340365	43.449028856	43.462776466	43.480556760	43.502325658	43.527940524	43.557593461	43.59111308	43.62880385
133	43.449115642	43.438218266	43.441391555	43.450080046	43.463827656	43.481607950	43.503396848	43.529045392	43.558708329	43.59222794	43.62985484
134	43.450166832	43.439269456	43.442442745	43.451131236	43.464878266	43.482658560	43.504447458	43.530196000	43.559858937	43.59337855	43.63090583
135	43.451218022	43.440320646	43.443493935	43.452182426	43.465931276	43.483711570	43.505500468	43.531249000	43.560911937	43.59443155	43.63195682
136	43.452269212	43.441371836	43.444545125	43.453233616	43.466980466	43.484761760	43.506551658	43.532300000	43.561964937	43.59548257	43.63300781
137	43.453320402	43.442423026	43.445596315	43.454284806	43.468033656	43.485813950	43.507602848	43.533350000	43.563015924	43.59653519	43.63405880
138	43.454371592	43.443474216	43.446647505	43.455362706	43.469111506	43.486891800	43.508654038	43.534400000	43.564066911	43.59758620	43.63510979
139	43.455422782	43.444525406	43.447698695	43.456397906	43.470145856	43.487926150	43.509705878	43.535450000	43.565117901	43.59863729	43.63616078
140	43.456473972	43.445576596	43.448749885	43.457448106	43.471196056	43.488976350	43.510757718	43.536500000	43.566168901	43.59968828	43.63721177
141	43.457525162	43.446627786	43.449799075	43.458497306	43.472246956	43.490027250	43.511808538	43.537550000	43.567220891	43.60073927	43.63826276
142	43.458576352	43.447678976	43.450850265	43.459548496	43.473297706	43.491078000	43.512859568	43.538600000	43.568272881	43.60179026	43.63931375
143	43.459627542	43.448730166	43.451901455	43.460599686	43.474348456	43.492128450	43.513910098	43.539650000	43.569324871	43.60284125	43.64036474
144	43.460678732	43.449781356	43.452952645	43.461658916	43.475399306	43.493178900	43.514960638	43.540700000	43.570376861	43.60389224	43.64141573
145	43.461729922	43.450832546	43.454003835	43.462709106	43.476450156	43.494229300	43.516011178	43.541750000	43.571427851	43.60494323	43.64246672
146	43.462781112	43.451883736	43.455055025	43.463759276	43.477500706	43.495288750	43.517061768	43.542800000	43.572478841	43.60599422	43.64351771
147	43.463832302	43.452934926	43.456106215	43.464809426	43.478551256	43.496349250	43.518112308	43.543850000	43.573529831	43.60704521	43.64456870
148	43.464883492	43.453986116	43.457157405	43.465859576	43.479601806	43.497409750	43.519162848	43.544900000	43.574580821	43.60809620	43.64561969
149	43.465934682	43.455037306	43.458208595	43.466909726	43.480652356	43.498470250	43.520213388	43.545950000	43.575631811	43.60914719	43.64667068
150	43.466985872	43.456088496	43.459259785	43.467959876	43.481702906	43.499520750	43.521263928	43.547000000	43.576682801	43.61019818	43.64772167

$K_n \left(\frac{z}{\sqrt{q}} \right)$

q	0	1	2	3	4	5	6	7	8	9	10
151	10.117304468	10.120366752	10.123429036	10.126491320	10.129553604	10.132615888	10.135678172	10.138740456	10.141802740	10.144865024	10.147927308
152	10.109727770	10.112789954	10.115852138	10.118914322	10.121976506	10.125038690	10.128100874	10.131163058	10.134225242	10.137287426	10.140349610
153	10.102150482	10.105212666	10.108274850	10.111337034	10.114399218	10.117461402	10.120523586	10.123585770	10.126647954	10.129710138	10.132772322
154	10.094573194	10.097635378	10.100697562	10.103759746	10.106821930	10.109884114	10.112946298	10.116008482	10.119070666	10.122132850	10.125195034
155	10.087000000	10.090062184	10.093124368	10.096186552	10.099248736	10.102310920	10.105373104	10.108435288	10.111497472	10.114559656	10.117621840
156	10.080000000	10.083062184	10.086124368	10.089186552	10.092248736	10.095310920	10.098373104	10.101435288	10.104497472	10.107559656	10.110621840
157	10.073000000	10.076062184	10.079124368	10.082186552	10.085248736	10.088310920	10.091373104	10.094435288	10.097497472	10.100559656	10.103621840
158	10.066000000	10.069062184	10.072124368	10.075186552	10.078248736	10.081310920	10.084373104	10.087435288	10.090497472	10.093559656	10.096621840
159	10.059000000	10.062062184	10.065124368	10.068186552	10.071248736	10.074310920	10.077373104	10.080435288	10.083497472	10.086559656	10.089621840
160	10.052000000	10.055062184	10.058124368	10.061186552	10.064248736	10.067310920	10.070373104	10.073435288	10.076497472	10.079559656	10.082621840
161	10.045000000	10.048062184	10.051124368	10.054186552	10.057248736	10.060310920	10.063373104	10.066435288	10.069497472	10.072559656	10.075621840
162	10.038000000	10.041062184	10.044124368	10.047186552	10.050248736	10.053310920	10.056373104	10.059435288	10.062497472	10.065559656	10.068621840
163	10.031000000	10.034062184	10.037124368	10.040186552	10.043248736	10.046310920	10.049373104	10.052435288	10.055497472	10.058559656	10.061621840
164	10.024000000	10.027062184	10.030124368	10.033186552	10.036248736	10.039310920	10.042373104	10.045435288	10.048497472	10.051559656	10.054621840
165	10.017000000	10.020062184	10.023124368	10.026186552	10.029248736	10.032310920	10.035373104	10.038435288	10.041497472	10.044559656	10.047621840
166	10.010000000	10.013062184	10.016124368	10.019186552	10.022248736	10.025310920	10.028373104	10.031435288	10.034497472	10.037559656	10.040621840
167	10.003000000	10.006062184	10.009124368	10.012186552	10.015248736	10.018310920	10.021373104	10.024435288	10.027497472	10.030559656	10.033621840
168	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
169	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
170	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
171	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
172	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
173	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
174	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
175	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
176	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
177	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
178	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
179	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
180	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
181	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
182	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
183	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
184	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
185	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
186	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
187	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
188	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
189	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
190	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
191	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
192	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
193	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
194	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
195	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
196	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
197	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
198	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
199	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840
200	10.000000000	10.003062184	10.006124368	10.009186552	10.012248736	10.015310920	10.018373104	10.021435288	10.024497472	10.027559656	10.030621840

$$K_n \left(\frac{x}{\sqrt{q}} \right)$$

q	n	0	1	2	3	4	5	6	7	8	9	10
201	201	40.5450036873	40.5750019212	40.614178109	40.6633119469	40.7497860496	40.772551959	41.1253346514	41.1637322797	41.2265053590	41.3865270580	41.4604603114
202	202	40.5315778668	40.5615761055	40.6002442693	40.6473194161	40.7347860496	40.757551959	41.1659333959	41.2043313959	41.27113410929	41.4313578194	41.5052842288
203	203	40.5284129638	40.5584112025	40.5970794161	40.6441545628	40.7316210961	40.754386915	41.1623113959	41.2007093959	41.26751210929	41.4277358194	41.5016622288
204	204	40.5252480607	40.5552463000	40.5938355136	40.6409106604	40.7282771947	40.751043094	41.1591313959	41.1975293959	41.26433210929	41.4245558194	41.4984822288
205	205	40.5220831576	40.5520813969	40.5906706105	40.6377457572	40.7251122915	40.747878191	41.1559313959	41.1943293959	41.26113210929	41.4213558194	41.4952822288
206	206	40.5189182545	40.5489164938	40.5875057074	40.6345808541	40.7219473884	40.744713288	41.1527313959	41.1911293959	41.25793210929	41.4181558194	41.4920822288
207	207	40.5157533514	40.5457515907	40.5843408043	40.6314159510	40.7188074417	40.741573341	41.1495313959	41.1879293959	41.25473210929	41.4149558194	41.4888822288
208	208	40.5125884483	40.5425866876	40.5811759012	40.6282510479	40.7156429324	40.738408832	41.1463313959	41.1847293959	41.25153210929	41.4117558194	41.4856822288
209	209	40.5094235452	40.5394217845	40.5780109981	40.6250861448	40.7124920231	40.735257923	41.1431313959	41.1815293959	41.24833210929	41.4105558194	41.4844822288
210	210	40.5062626421	40.5362608814	40.5748490950	40.6219242417	40.7103861036	40.733152004	41.1399313959	41.1783293959	41.24513210929	41.4093558194	41.4812822288
211	211	40.5031017390	40.5330999783	40.5716881919	40.6187633386	40.7072751935	40.730041094	41.1367313959	41.1751293959	41.24193210929	41.4081558194	41.4790822288
212	212	40.5000408359	40.5299390752	40.5685272888	40.6156024355	40.7041642822	40.726930183	41.1335313959	41.1719293959	41.23873210929	41.4069558194	41.4778822288
213	213	40.4969800328	40.5268782721	40.5654664857	40.6125255322	40.7010854709	40.723851372	41.1303313959	41.1687293959	41.23553210929	41.4057558194	41.4766822288
214	214	40.4939192297	40.5238174690	40.5624056819	40.6094006786	40.6980118615	40.720762273	41.1271313959	41.1655293959	41.23233210929	41.4045558194	41.4754822288
215	215	40.4908584266	40.5207566659	40.5593448788	40.6063396755	40.6950508584	40.717603167	41.1239313959	41.1623293959	41.22913210929	41.4033558194	41.4742822288
216	216	40.4877976235	40.5176958628	40.5562840750	40.6032784838	40.6919896667	40.714454058	41.1207313959	41.1591293959	41.22593210929	41.4021558194	41.4730822288
217	217	40.4847368204	40.5146350601	40.5531232723	40.6002172916	40.6889288596	40.711304949	41.1175313959	41.1559293959	41.22273210929	41.4009558194	41.4718822288
218	218	40.4816760173	40.5115742574	40.5500624795	40.5971464968	40.6860380525	40.708154840	41.1143313959	41.1527293959	41.21953210929	41.4007558194	41.4706822288
219	219	40.4786152142	40.5085134545	40.5470016666	40.5942258839	40.6831482458	40.705004731	41.1111313959	41.1495293959	41.21633210929	41.4005558194	41.4694822288
220	220	40.4755544111	40.5054526514	40.5439408635	40.5911470912	40.6800580387	40.701854622	41.1079313959	41.1463293959	41.21313210929	41.4003558194	41.4682822288
221	221	40.4724936080	40.5023918483	40.5408800758	40.5880462881	40.6769680316	40.700704513	41.1047313959	41.1431293959	41.20993210929	41.4001558194	41.4670822288
222	222	40.4694328049	40.5003310452	40.5388692829	40.5859854901	40.6749080245	40.69961988	41.1015313959	41.1400293959	41.20773210929	41.4000558194	41.4658822288
223	223	40.4663720018	40.4972702421	40.5358084801	40.5839346974	40.672822369	40.69653868	41.0983313959	41.1368293959	41.20553210929	41.4000558194	41.4646822288
224	224	40.4633111987	40.4942094390	40.5327476792	40.5810299065	40.670736258	40.69444007	41.0951313959	41.1336293959	41.20233210929	41.4000558194	41.4634822288
225	225	40.4602503956	40.4911486349	40.5296868685	40.5780301138	40.668644847	40.69234886	41.0919313959	41.1304293959	41.20013210929	41.4000558194	41.4622822288
226	226	40.4571895925	40.4880878328	40.5276260614	40.5759693191	40.666559733	40.68926375	41.0887313959	41.1272293959	41.19793210929	41.4000558194	41.4610822288
227	227	40.4541287894	40.4850270297	40.5255652501	40.5739087764	40.664474647	40.68717867	41.0855313959	41.1240293959	41.19473210929	41.4000558194	41.4598822288
228	228	40.4510679863	40.4820662260	40.5235044414	40.5718482317	40.662385531	40.68508956	41.0823313959	41.1208293959	41.19253210929	41.4000558194	41.4586822288
229	229	40.4480071832	40.4790054235	40.5214436328	40.5697877270	40.660296420	40.68290045	41.0791313959	41.1176293959	41.19033210929	41.4000558194	41.4574822288
230	230	40.4449463801	40.4760446204	40.5193828241	40.5677269214	40.658207309	40.68081134	41.0759313959	41.1144293959	41.18713210929	41.4000558194	41.4562822288
231	231	40.4418855770	40.4730838607	40.5173220156	40.5656669189	40.656118198	40.67872218	41.0727313959	41.1112293959	41.18483210929	41.4000558194	41.4550822288
232	232	40.4388247739	40.4700230574	40.5152612062	40.5636060202	40.654029087	40.67663317	41.0695313959	41.1080293959	41.18263210929	41.4000558194	41.4538822288
233	233	40.4357639708	40.4670622483	40.5131995977	40.5615951221	40.651940176	40.67454416	41.0663313959	41.1048293959	41.18043210929	41.4000558194	41.4526822288
234	234	40.4327031677	40.4640014452	40.5111387886	40.5595842264	40.649851165	40.67245515	41.0631313959	41.1016293959	41.17823210929	41.4000558194	41.4514822288
235	235	40.4296423646	40.4610407221	40.5090780795	40.5575732678	40.647762054	40.67036604	41.0599313959	41.0984293959	41.17603210929	41.4000558194	41.4502822288
236	236	40.4265815615	40.4579799990	40.5070172704	40.5555124661	40.645672943	40.66827003	41.0567313959	41.0952293959	41.17383210929	41.4000558194	41.4490822288
237	237	40.4235207584	40.4549192859	40.5049564718	40.5534516672	40.643583832	40.66618312	41.0535313959	41.0920293959	41.17163210929	41.4000558194	41.4478822288
238	238	40.4204600553	40.4518584828	40.5028956687	40.5513908681	40.641494721	40.66409401	41.0503313959	41.0888293959	41.16943210929	41.4000558194	41.4466822288
239	239	40.4173993522	40.4488077707	40.5008348652	40.5493299656	40.639405610	40.66200490	41.0471313959	41.0856293959	41.16723210929	41.4000558194	41.4454822288
240	240	40.4143386491	40.4458470676	40.5007740581	40.5462690585	40.637316500	40.65991519	41.0439313959	41.0824293959	41.16503210929	41.4000558194	41.4442822288
241	241	40.4112779460	40.4427863845	40.5007132510	40.5432281089	40.635227491	40.65782668	41.0407313959	41.0792293959	41.16283210929	41.4000558194	41.4430822288
242	242	40.4082172429	40.4397256814	40.5006524460	40.5401870578	40.633138482	40.65573587	41.0375313959	41.0760293959	41.16063210929	41.4000558194	41.4418822288
243	243	40.4051565398	40.4366650783	40.5005916411	40.5371362547	40.631049373	40.65364706	41.0343313959	41.0728293959	41.15843210929	41.4000558194	41.4406822288
244	244	40.4020958367	40.4336043752	40.5005308362	40.5340750412	40.628960264	40.65155795	41.0311313959	41.0696293959	41.15623210929	41.4000558194	41.4394822288
245	245	40.4000351336	40.4315436721	40.5004700313	40.5320143385	40.626871155	40.64946884	41.0279313959	41.0654293959	41.15403210929	41.4000558194	41.4382822288
246	246	40.3979744305	40.4294829690	40.5004092264	40.5299536358	40.624782046	40.64737973	41.0247313959	41.0632293959	41.15183210929	41.4000558194	41.4370822288
247	247	40.3959137274	40.4274222659	40.5003484215	40.5278929309	40.622692937	40.64529062	41.0215313959	41.0610293959	41.14963210929	41.4000558194	41.4358822288
248	248	40.3938530243	40.4253615628	40.5002876166	40.5258322260	40.620603828	40.64320151	41.0183313959	41.0588293959	41.14743210929	41.4000558194	41.4346822288
249	249	40.3917923212	40.4233008597	40.5002268117	40.5237715211	40.618514719	40.64111240	41.0151313959	41.0566293959	41.14523210929	41.4000558194	41.4334822288
250	250	40.3897316181	40.4212401566	40.5001660068	40.5217108162	40.616425610	40.63902329	41.0119313959	41.0544293959	41.14303210929	41.4000558194	41.4322822288

n	0	1	2	3	4	5	6	7	8	9	10
1	50.3931751797	51.145596657	50.559296033	51.311696707	50.281912640	51.013463959	50.277413983	55.118949706	56.149000084	57.65662048	59.113549676
2	50.1271577977	50.801201029	50.281912640	51.013463959	50.342400495	51.173267617	52.361277659	53.632138434	54.902111764	56.17303070	57.44584551
3	50.1434347082	50.172644471	50.342400495	51.013463959	50.921448257	51.342400495	52.361277659	53.632138434	54.902111764	56.17303070	57.44584551
4	50.1017447082	50.127157797	50.172644471	50.342400495	50.921448257	51.342400495	52.361277659	53.632138434	54.902111764	56.17303070	57.44584551
5	50.752049668	50.9011176682	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257	51.342400495	52.361277659	53.632138434	54.902111764
6	50.716957668	50.863011798	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257	51.342400495	52.361277659	53.632138434	54.902111764
7	50.716957668	50.863011798	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257	51.342400495	52.361277659	53.632138434	54.902111764
8	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257	51.342400495	52.361277659	53.632138434	54.902111764
9	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257	51.342400495	52.361277659
10	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
11	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
12	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
13	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
14	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
15	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
16	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
17	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
18	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
19	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
20	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
21	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
22	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
23	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
24	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
25	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
26	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
27	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
28	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
29	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
30	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
31	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
32	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
33	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
34	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
35	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
36	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
37	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
38	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
39	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
40	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
41	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
42	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
43	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
44	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
45	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
46	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
47	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
48	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
49	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257
50	50.828661316	50.898661316	50.5929668314	50.6683136718	50.3630436718	50.4360136718	50.101744708	50.127157797	50.172644471	50.342400495	50.921448257

$K_n(\frac{2}{3}\sqrt{q})$

q	0	1	2	3	4	5	6	7	8	9	10
51	47.2519514926	47.2711409374	47.3275753447	47.4466607459	47.6509379508	47.1180462707	48.288416068	48.183951023	49.1127630846	49.289327687	49.809337940
52	47.2358003279	47.2510576003	47.3073904218	47.4263136243	47.6313624343	47.9850792931	48.2056325987	48.345955039	49.1011288803	49.2577159517	49.7194336592
53	47.2184449137	47.2348094515	47.2912394185	47.410188126	47.6157687836	48.1869752876	48.3868137172	48.5398121172	49.289118712	49.4513287428	49.9161373552
54	47.20042491738	47.2180012173	47.27585997407	47.3948606596	47.5986870044	48.1721394760	48.3575759166	48.5194760166	49.268287462	49.4392287462	49.8963305054
55	47.1817575811	47.1999010181	47.2580483271	47.3770807581	47.580958371	48.1546656756	48.3317654499	48.4936656756	49.2464040366	49.4174040366	49.8735051616
56	47.16248023109	47.1811749510	47.2402521347	47.3592828499	47.5634878669	48.1382914444	48.3151764499	48.4769561632	49.2355956163	49.4075956163	49.8636329299
57	47.1427323109	47.16248023109	47.2220521347	47.3410811556	47.5452021386	48.1207921804	48.2987921804	48.4605721804	49.2247921804	49.3967921804	49.852823307
58	47.12248023109	47.1427323109	47.20248023109	47.321531367	47.525651367	48.1027921804	48.2807921804	48.4425721804	49.2139921804	49.3859921804	49.842023307
59	47.10218023109	47.12248023109	47.18248023109	47.301531367	47.505651367	48.0827921804	48.2607921804	48.4225721804	49.2031921804	49.3701921804	49.82623307
60	47.08188023109	47.10218023109	47.16218023109	47.281231367	47.485351367	48.0627921804	48.2407921804	48.4025721804	49.1923921804	49.3593921804	49.81543307
61	47.06158023109	47.08188023109	47.14218023109	47.261231367	47.465351367	48.0427921804	48.2207921804	48.3825721804	49.1815921804	49.3485921804	49.80463307
62	47.04128023109	47.06158023109	47.12218023109	47.241231367	47.445351367	48.0227921804	48.2007921804	48.3625721804	49.1707921804	49.3377921804	49.79373307
63	47.02098023109	47.04128023109	47.10218023109	47.221231367	47.425351367	48.0027921804	48.1807921804	48.3425721804	49.1599921804	49.3269921804	49.78293307
64	47.00068023109	47.02098023109	47.08188023109	47.201231367	47.405351367	47.9827921804	48.1607921804	48.3225721804	49.1491921804	49.3161921804	49.77213307
65	46.98038023109	47.00068023109	47.06158023109	47.181231367	47.385351367	47.9627921804	48.1407921804	48.3025721804	49.1383921804	49.3053921804	49.76133307
66	46.96008023109	46.98038023109	47.04128023109	47.161231367	47.365351367	47.9427921804	48.1207921804	48.2825721804	49.1275921804	49.2945921804	49.75053307
67	46.93978023109	46.96008023109	47.02098023109	47.141231367	47.345351367	47.9227921804	48.1007921804	48.2625721804	49.1167921804	49.2837921804	49.73973307
68	46.91948023109	46.93978023109	47.00068023109	47.121231367	47.325351367	47.9027921804	48.0807921804	48.2425721804	49.1059921804	49.2729921804	49.72893307
69	46.89918023109	46.91948023109	46.98038023109	47.101231367	47.305351367	47.8827921804	48.0607921804	48.2225721804	49.0951921804	49.2621921804	49.71813307
70	46.87888023109	46.89918023109	46.96008023109	47.081231367	47.285351367	47.8627921804	48.0407921804	48.2025721804	49.0843921804	49.2513921804	49.70733307
71	46.85858023109	46.87888023109	46.93978023109	47.061231367	47.265351367	47.8427921804	48.0207921804	48.1825721804	49.0735921804	49.2405921804	49.69653307
72	46.83828023109	46.85858023109	46.91948023109	47.041231367	47.245351367	47.8227921804	48.0007921804	48.1625721804	49.0627921804	49.2297921804	49.68573307
73	46.81798023109	46.83828023109	46.89918023109	47.021231367	47.225351367	47.8027921804	47.9807921804	48.1425721804	49.0519921804	49.2189921804	49.67493307
74	46.79768023109	46.81798023109	46.87888023109	47.001231367	47.205351367	47.7827921804	47.9607921804	48.1225721804	49.0411921804	49.2081921804	49.66413307
75	46.77738023109	46.79768023109	46.85858023109	46.981231367	47.185351367	47.7627921804	47.9407921804	48.1025721804	49.0303921804	49.1973921804	49.65333307
76	46.75708023109	46.77738023109	46.83828023109	46.961231367	47.165351367	47.7427921804	47.9207921804	48.0825721804	49.0195921804	49.1865921804	49.64253307
77	46.73678023109	46.75708023109	46.81798023109	46.941231367	47.145351367	47.7227921804	47.9007921804	48.0625721804	49.0087921804	49.1757921804	49.63173307
78	46.71648023109	46.73678023109	46.79768023109	46.921231367	47.125351367	47.7027921804	47.8807921804	48.0425721804	48.9979921804	49.1649921804	49.62093307
79	46.69618023109	46.71648023109	46.77738023109	46.901231367	47.105351367	47.6827921804	47.8607921804	48.0225721804	48.9871921804	49.1541921804	49.61013307
80	46.67588023109	46.69618023109	46.75708023109	46.881231367	47.085351367	47.6627921804	47.8407921804	48.0025721804	48.9763921804	49.1433921804	49.59933307
81	46.65558023109	46.67588023109	46.73678023109	46.861231367	47.065351367	47.6427921804	47.8207921804	47.9825721804	48.9655921804	49.1325921804	49.58853307
82	46.63528023109	46.65558023109	46.71648023109	46.841231367	47.045351367	47.6227921804	47.8007921804	47.9625721804	48.9547921804	49.1217921804	49.57773307
83	46.61498023109	46.63528023109	46.69618023109	46.821231367	47.025351367	47.6027921804	47.7807921804	47.9425721804	48.9439921804	49.1109921804	49.56693307
84	46.59468023109	46.61498023109	46.67588023109	46.801231367	47.005351367	47.5827921804	47.7607921804	47.9225721804	48.9331921804	49.1001921804	49.55613307
85	46.57438023109	46.59468023109	46.65558023109	46.781231367	46.985351367	47.5627921804	47.7407921804	47.9025721804	48.9223921804	49.0893921804	49.54533307
86	46.55408023109	46.57438023109	46.63528023109	46.761231367	46.965351367	47.5427921804	47.7207921804	47.8825721804	48.9115921804	49.0785921804	49.53453307
87	46.53378023109	46.55408023109	46.61498023109	46.741231367	46.945351367	47.5227921804	47.7007921804	47.8625721804	48.9007921804	49.0677921804	49.52373307
88	46.51348023109	46.53378023109	46.59468023109	46.721231367	46.925351367	47.5027921804	47.6807921804	47.8425721804	48.8899921804	49.0569921804	49.51293307
89	46.49318023109	46.51348023109	46.57438023109	46.701231367	46.905351367	47.4827921804	47.6607921804	47.8225721804	48.8791921804	49.0461921804	49.50213307
90	46.47288023109	46.49318023109	46.55408023109	46.681231367	46.885351367	47.4627921804	47.6407921804	47.8025721804	48.8683921804	49.0353921804	49.49133307
91	46.45258023109	46.47288023109	46.53378023109	46.661231367	46.865351367	47.4427921804	47.6207921804	47.7825721804	48.8575921804	49.0245921804	49.48053307
92	46.43228023109	46.45258023109	46.51348023109	46.641231367	46.845351367	47.4227921804	47.6007921804	47.7625721804	48.8467921804	49.0137921804	49.46973307
93	46.41198023109	46.43228023109	46.49318023109	46.621231367	46.825351367	47.4027921804	47.5807921804	47.7425721804	48.8359921804	49.0029921804	49.45893307
94	46.39168023109	46.41198023109	46.47288023109	46.601231367	46.805351367	47.3827921804	47.5607921804	47.7225721804	48.8251921804	48.9921921804	49.44813307
95	46.37138023109	46.39168023109	46.45258023109	46.581231367	46.785351367	47.3627921804	47.5407921804	47.7025721804	48.8143921804	48.9813921804	49.43733307
96	46.35108023109	46.37138023109	46.43228023109	46.561231367	46.765351367	47.3427921804	47.5207921804	47.6825721804	48.8035921804	48.9705921804	49.42653307
97	46.33078023109	46.35108023109	46.41198023109	46.541231367	46.745351367	47.3227921804	47.5007921804	47.6625721804	48.7927921804	48.9597921804	49.41573307
98	46.31048023109	46.33078023109	46.39168023109	46.521231367	46.725351367	47.3027921804	47.4807921804	47.6425721804	48.7819921804	48.9489921804	49.40493307
99	46.29018023109	46.31048023109	46.37138023109	46.501231367	46.705351367	47.2827921804	47.4607921804	47.6225721804	48.7711921804	48.9381921804	49.39413307
100	46.26988023109	46.29018023109	46.35108023109	46.481231367	46.685351367	47.2627921804	47.4407921804	47.6025721804	48.7603921804	48.9273921804	49.38333307

[illegible]

$K_n(\sqrt{x})$

n	0	1	2	3	4	5	6	7	8	9	10
151	44.892574471	44.926622636	45.1016619829	45.1248880221	45.1610933761	45.2225515000	45.3371588334	45.5392467893	45.9245566493	46.1689756159	46.3279764044
152	44.854038053	44.8865167852	45.09136649415	45.1197666336	45.1346099415	45.2153168766	45.3216969827	45.5137775595	45.8783919473	46.1623444552	46.312372198
153	44.93671701	44.8426716552	44.9442310999	45.1141069396	45.2051314569	45.2897141138	45.3689714118	45.4897917118	45.6483763661	46.1320780715	46.2738807765
154	44.7782597966	44.8177132829	44.9171310601	45.1094966552	45.1340966552	45.1586966552	45.1832966552	45.2078966552	45.2324966552	45.2570966552	45.2816966552
155	44.7601316927	44.8006136927	44.895442002	44.9767132829	45.0580132829	45.1393132829	45.2206132829	45.3019132829	45.3832132829	45.4645132829	45.5458132829
156	44.665189398	44.712348048	44.794682155	44.944653976	45.1238937418	45.1789778315	45.2653465906	45.402016036	45.710652706	46.129934137	46.231410249
157	44.657288083	44.681811563	44.708606359	44.913286061	45.1213925732	45.1705081131	45.2451045387	45.382320573	45.686664073	46.121331771	46.231410249
158	44.657334177	44.659318109	44.7284114231	44.8763101784	45.1127186661	45.1554248189	45.2303321274	45.348220573	45.6171895868	46.112816155	46.220595436
159	44.650383866	44.6594501774	44.6974466721	44.86713145	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
160	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
161	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
162	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
163	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
164	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
165	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
166	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
167	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
168	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
169	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
170	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
171	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
172	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
173	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
174	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
175	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
176	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
177	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
178	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
179	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
180	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
181	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
182	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
183	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
184	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
185	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
186	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
187	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
188	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
189	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
190	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
191	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
192	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
193	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
194	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
195	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
196	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
197	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
198	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
199	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436
200	44.577330891	44.5949073145	44.6399297346	44.8199297346	45.1051375189	45.1451361380	45.217961342	45.334213418	45.6171895868	46.112816155	46.220595436

$K_n(\frac{\pi}{2}, \sqrt{q})$	0	1	2	3	4	5	6	7	8	9	10
1	11.1107573342	11.188769481	11.1310705692	11.154184562	11.1931815608	11.2495868396	11.3674194176	11.553359601	11.8911111427	15.1577000718	15.4781815608
2	11.1107553257	11.1417175042	11.265134194	11.483134962	11.109210950	11.215315465	11.344134194	11.510797138	11.8102719382	15.1380123887	15.4849278101
3	11.102675619	11.116876466	11.168566707	11.18713096193	11.1759700470	11.2282201619	11.321566693	11.4901102684	11.7813869241	15.1328693241	15.4827932422
4	11.9884790105	11.102866700	11.134667007	11.1271372738	11.1553270470	11.2003086190	11.3126264556	11.4702254287	11.7513212386	15.1281969341	15.4827932422
5	11.921889404	11.9316804780	11.1082697003	11.1221372738	11.1592607716	11.2171581954	11.2995909136	11.4512015256	11.7801827395	15.127857395	15.4827932422
6	11.8826153996	11.9117330614	11.1023684137	11.117578747	11.15715912	11.1957028839	11.2767110282	11.435952867	11.6904190387	15.1166190387	15.4827932422
7	11.8716217895	11.900766693	11.1023684137	11.117578747	11.15715912	11.1957028839	11.2767110282	11.435952867	11.6904190387	15.1166190387	15.4827932422
8	11.8716217895	11.900766693	11.1023684137	11.117578747	11.15715912	11.1957028839	11.2767110282	11.435952867	11.6904190387	15.1166190387	15.4827932422
9	11.8716217895	11.900766693	11.1023684137	11.117578747	11.15715912	11.1957028839	11.2767110282	11.435952867	11.6904190387	15.1166190387	15.4827932422
10	11.8716217895	11.900766693	11.1023684137	11.117578747	11.15715912	11.1957028839	11.2767110282	11.435952867	11.6904190387	15.1166190387	15.4827932422
11	11.8716217895	11.900766693	11.1023684137	11.117578747	11.15715912	11.1957028839	11.2767110282	11.435952867	11.6904190387	15.1166190387	15.4827932422
12	11.8716217895	11.900766693	11.1023684137	11.117578747	11.15715912	11.1957028839	11.2767110282	11.435952867	11.6904190387	15.1166190387	15.4827932422
13	11.8716217895	11.900766693	11.1023684137	11.117578747	11.15715912	11.1957028839	11.2767110282	11.435952867	11.6904190387	15.1166190387	15.4827932422
14	11.8716217895	11.900766693	11.1023684137	11.117578747	11.15715912	11.1957028839	11.2767110282	11.435952867	11.6904190387	15.1166190387	15.4827932422
15	11.8716217895	11.900766693	11.1023684137	11.117578747	11.15715912	11.1957028839	11.2767110282	11.435952867	11.6904190387	15.1166190387	15.4827932422
16	11.8716217895	11.900766693	11.1023684137	11.117578747	11.15715912	11.1957028839	11.2767110282	11.435952867	11.6904190387	15.1166190387	15.4827932422
17	11.8716217895	11.900766693	11.1023684137	11.117578747	11.15715912	11.1957028839	11.2767110282	11.435952867	11.6904190387	15.1166190387	15.4827932422
18	11.8716217895	11.900766693	11.1023684137	11.117578747	11.15715912	11.1957028839	11.2767110282	11.435952867	11.6904190387	15.1166190387	15.4827932422
19	11.8716217895	11.900766693	11.1023684137	11.117578747	11.15715912	11.1957028839	11.2767110282	11.435952867	11.6904190387	15.1166190387	15.4827932422
20	11.8716217895	11.900766693	11.1023684137	11.117578747	11.15715912	11.1957028839	11.2767110282	11.435952867	11.6904190387	15.1166190387	15.4827932422

$$K_n(\sqrt{x})$$

q	n	0	1	2	3	4	5	6	7	8	9	10
251	43	190408726	43.16604709	43.214043750	43.247676004	43.263613742	43.269072018	43.271387039	43.275472049	43.2803957836	44.187364932	44.3315870342
252	43	18404185000	43.1095008025	43.2086846990	43.2392712217	43.253027379	43.260370060	43.263037039	43.2654792313	43.267193213	44.187379132	44.33181871327
253	43	1779046500	43.1079019527	43.1982800192	43.231173393	43.248170539	43.257167417	43.260000019	43.26229675	43.26411716796	44.1873914194	44.33205266687
254	43	17179458000	43.1170613110	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187399674	44.332295977
255	43	1657044100	43.1261311912	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187407971	44.332539297
256	43	159544132	43.1352248139	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187416273	44.332782617
257	43	153434132	43.1443182	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187424575	44.333025937
258	43	147324132	43.1534132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187432877	44.333269257
259	43	141214132	43.1625132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187441179	44.333512577
260	43	135104132	43.1716132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187449481	44.333755897
261	43	128994132	43.1807132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187457783	44.334000017
262	43	122884132	43.1898132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187466085	44.334244137
263	43	116774132	43.1989132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187474387	44.334488257
264	43	110664132	43.2080132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187482689	44.334732377
265	43	104554132	43.2171132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187490991	44.334976497
266	43	98444132	43.2262132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187499293	44.335220617
267	43	92334132	43.2353132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187507595	44.335464737
268	43	86224132	43.2444132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187515897	44.335708857
269	43	80114132	43.2535132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187524199	44.335952977
270	43	74004132	43.2626132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187532501	44.336197097
271	43	67894132	43.2717132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187540803	44.336441217
272	43	61784132	43.2808132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187549105	44.336685337
273	43	55674132	43.2899132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187557407	44.336929457
274	43	49564132	43.2990132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187565709	44.337173577
275	43	43454132	43.3081132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187574011	44.337417697
276	43	37344132	43.3172132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187582313	44.337661817
277	43	31234132	43.3263132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187590615	44.337905937
278	43	25124132	43.3354132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187598917	44.338150057
279	43	19014132	43.3445132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187607219	44.338394177
280	43	12904132	43.3536132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187615521	44.338638297
281	43	10794132	43.3627132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187623823	44.338882417
282	43	8684132	43.3718132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187632125	44.339126537
283	43	6574132	43.3809132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187640427	44.339370657
284	43	4464132	43.3900132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187648729	44.339614777
285	43	2354132	43.3991132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187657031	44.339858897
286	43	244	43.4082132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187665333	44.340103017
287	43	244	43.4173132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187673635	44.340347137
288	43	244	43.4264132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187681937	44.340591257
289	43	244	43.4355132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187690239	44.340835377
290	43	244	43.4446132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187698541	44.341079497
291	43	244	43.4537132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187706843	44.341323617
292	43	244	43.4628132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187715145	44.341567737
293	43	244	43.4719132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187723447	44.341811857
294	43	244	43.4810132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187731749	44.342055977
295	43	244	43.4901132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187740051	44.342300097
296	43	244	43.4992132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187748353	44.342544217
297	43	244	43.5083132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187756655	44.342788337
298	43	244	43.5174132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187764957	44.343032457
299	43	244	43.5265132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187773259	44.343276577
300	43	244	43.5356132	43.1979600192	43.231706192	43.2493366597	43.2584660213	43.26148888786	43.26399569	43.265990674	44.187781561	44.343520697

$$K(n + \frac{1}{2}) (\frac{1}{2} \sqrt{q})$$

n	0	1	2	3	4	5	6	7	8	9	10
1	50.207815764	50.340219829	50.857615789	51.307020989	52.145193449	52.863756631	53.619425294	54.323626954	55.503673725	56.506311790	57.671073250
2	49.1329507365	49.265373689	49.7827987010	50.295911680	50.799511680	51.266070758	51.826070758	52.384270758	52.942470758	53.498670758	54.054870758
3	48.0580853465	48.190508300	48.7079233120	49.215036291	49.722149270	50.229262249	50.736375228	51.243488207	51.750601186	52.257714165	52.764827144
4	46.9831999565	47.115622910	47.6300379220	48.137150901	48.644263880	49.151376859	49.658489838	50.165602817	50.672715796	51.179828775	51.686941754
5	45.9083145565	46.040737510	46.5551525220	47.062265501	47.569378480	48.076491459	48.583604438	49.090717417	49.597830396	50.104943375	50.612056354
6	44.8334291565	44.965852110	45.4802671220	45.987380101	46.494493080	47.001606059	47.508719038	48.015832017	48.522944996	49.030057975	49.537170954
7	43.7585437565	43.890966710	44.4053817220	44.912494701	45.419607680	45.926720659	46.433833638	46.940946617	47.448059596	47.955172575	48.462285554
8	42.6836583565	42.816081310	43.3304963220	43.837609301	44.344722280	44.851835259	45.358948238	45.866061217	46.373174196	46.880287175	47.387400154
9	41.6087729565	41.741195910	42.2556109220	42.762723901	43.269836880	43.776949859	44.284062838	44.791175817	45.298288796	45.805401775	46.312514754
10	40.5338875565	40.666310510	41.1807255220	41.687838501	42.194951480	42.702064459	43.209177438	43.716290417	44.223403396	44.730516375	45.237629354
11	39.4589921565	39.591415110	40.1058301220	40.612943101	41.120056080	41.627169059	42.134282038	42.641395017	43.148507996	43.655620975	44.162733954
12	38.3840967565	38.516519710	39.0309347220	39.538047701	40.045160680	40.552273659	41.059386638	41.566499617	42.073612596	42.580725575	43.087838554
13	37.3092013565	37.441624310	37.9560393220	38.463152301	38.970265280	39.477378259	39.984491238	40.491604217	40.998717196	41.505830175	42.012943154
14	36.2343059565	36.366728910	36.8811439220	37.388256901	37.895369880	38.402482859	38.909595838	39.416708817	39.923821796	40.430934775	40.938047754
15	35.1594105565	35.291833510	35.8062485220	36.313361501	36.820474480	37.327587459	37.834700438	38.341813417	38.848926396	39.356039375	39.863152354
16	34.0845151565	34.216938110	34.7313531220	35.238466101	35.745579080	36.252692059	36.759805038	37.266918017	37.774030996	38.281143975	38.788256954
17	33.0096197565	33.142042710	33.6564577220	34.163570701	34.670683680	35.177796659	35.684909638	36.192022617	36.699135596	37.206248575	37.713361554
18	31.9347243565	32.067147310	32.5815623220	33.088675301	33.595788280	34.102901259	34.610014238	35.117127217	35.624240196	36.131353175	36.638466154
19	30.8598289565	30.992251910	31.5066669220	32.013779901	32.520892880	33.028005859	33.535118838	34.042231817	34.549344796	35.056457775	35.563570754
20	29.7849335565	29.917356510	30.4317715220	30.938884501	31.445997480	31.953110459	32.460223438	32.967336417	33.474449396	33.981562375	34.488675354
21	28.7100381565	28.842461110	29.3568761220	29.863989101	30.371102080	30.878215059	31.385328038	31.892441017	32.399553996	32.906666975	33.413779954
22	27.6351427565	27.767565710	28.2819807220	28.789093701	29.296206680	29.803319659	30.310432638	30.817545617	31.324658596	31.831771575	32.338884554
23	26.5602473565	26.692670310	27.2070853220	27.714198301	28.221311280	28.728424259	29.235537238	29.742650217	30.249763196	30.756876175	31.263989154
24	25.4853519565	25.617774910	26.1321899220	26.639302901	27.146415880	27.653528859	28.160641838	28.667754817	29.174867796	29.681980775	30.189093754
25	24.4104565565	24.542879510	25.0572945220	25.564407501	26.071520480	26.578633459	27.085746438	27.592859417	28.100072396	28.607185375	29.114298354
26	23.3355611565	23.467984110	23.9823991220	24.489512101	24.996625080	25.503738059	26.010851038	26.517964017	27.025076996	27.532189975	28.039302954
27	22.2606657565	22.393088710	22.9075037220	23.414616701	23.921729680	24.428842659	24.935955638	25.443068617	25.950181596	26.457294575	26.964407554
28	21.1857703565	21.318193310	21.8326083220	22.339721301	22.846834280	23.353947259	23.861060238	24.368173217	24.875286196	25.382399175	25.889512154
29	20.1108749565	20.243297910	20.7577129220	21.264825901	21.771938880	22.279051859	22.786164838	23.293277817	23.800390796	24.307503775	24.814616754
30	19.0359795565	19.168402510	19.6828175220	20.189930501	20.697043480	21.204156459	21.711269438	22.218382417	22.725495396	23.232608375	23.739721354
31	17.9610841565	18.093507110	18.6079221220	19.115035101	19.622148080	20.129261059	20.636374038	21.143487017	21.650600996	22.157713975	22.664826954
32	16.8861887565	17.018611710	17.5330267220	18.040139701	18.547252680	19.054365659	19.561478638	20.068591617	20.575704596	21.082817575	21.589930554
33	15.8112933565	15.943716310	16.4581313220	16.965244301	17.472357280	17.979470259	18.486583238	18.993696217	19.500809196	20.007922175	20.515035154
34	14.7363979565	14.868820910	15.3832359220	15.890348901	16.397461880	16.904574859	17.411687838	17.918800817	18.425913796	18.933026775	19.440139754
35	13.6615025565	13.793925510	14.3083405220	14.815453501	15.322566480	15.829679459	16.336792438	16.843905417	17.351018396	17.858131375	18.365244354
36	12.5866071565	12.719030110	13.2334451220	13.740558101	14.247671080	14.754784059	15.261897038	15.769010017	16.276122996	16.783235975	17.290348954
37	11.5117117565	11.644134710	12.1585497220	12.665662701	13.172775680	13.679888659	14.187001638	14.694114617	15.201227596	15.708340575	16.215453554
38	10.4368163565	10.569239310	11.0836543220	11.590767301	12.097880280	12.604993259	13.112106238	13.619219217	14.126332196	14.633445175	15.140558154
39	9.3619209565	9.494343910	10.0087589220	10.515871901	11.022984880	11.530097859	12.037210838	12.544323817	13.051436796	13.558549775	14.065662754
40	8.2870255565	8.419448510	8.9338635220	9.440976501	9.948089480	10.455202459	10.962315438	11.469428417	11.976541396	12.483654375	12.990767354
41	7.2121301565	7.344553110	7.8589681220	8.366081101	8.873194080	9.380307059	9.887420038	10.394533017	10.901645996	11.408758975	11.915871954
42	6.1372347565	6.269657710	6.7840727220	7.291185701	7.798298680	8.305411659	8.812524638	9.319637617	9.826750596	10.333863575	10.840976554
43	5.0623393565	5.194762310	5.7091773220	6.216290301	6.723403280	7.230516259	7.737629238	8.244742217	8.751855196	9.258968175	9.766081154
44	3.9874439565	4.119866910	4.6342819220	5.141394901	5.648507880	6.155620859	6.662733838	7.169846817	7.676959796	8.184072775	8.691185754
45	2.9125485565	3.044971510	3.5593865220	4.066499501	4.573612480	5.080725459	5.587838438	6.094951417	6.602064396	7.109177375	7.616290354
46	1.8376531565	1.970076110	2.4844911220	2.991604101	3.498717080	4.005830059	4.512943038	5.020056017	5.527168996	6.034281975	6.541394954
47	0.7627577565	0.895180710	1.4095957220	1.916708701	2.423821680	2.930934659	3.438047638	3.945160617	4.452273596	4.959386575	5.466499554
48	-0.3121377565	-0.179714710	0.3353007220	0.842413701	1.349526680	1.856639659	2.363752638	2.870865617	3.377978596	3.885091575	4.392204554
49	-1.3872423565	-1.254819310	-0.7403043220	-0.233191301	0.273921680	0.781034659	1.288147638	1.795260617	2.302373596	2.809486575	3.316599554
50	-2.4623469565	-2.330023910	-1.8155089220	-1.308395901	-0.801282880	-0.294169859	0.213043175	0.720156154	1.227269133	1.734382112	2.241495091

$$K_{(n+1/2)}\left(\frac{x}{q}\right)$$

q	0	1	2	3	4	5	6	7	8	9	10
51	5.527706610	5.5475716586	5.569124704	5.591683770	5.615234675	5.639765966	5.665193624	5.691523610	5.718753610	5.746883610	5.774913610
52	5.540420668	5.560285668	5.581734704	5.604773780	5.629403686	5.655623610	5.683433610	5.712843610	5.743853610	5.775463610	5.807673610
53	5.553030668	5.572895668	5.594344704	5.617383780	5.641913686	5.667033610	5.692743610	5.719053610	5.745963610	5.773473610	5.801583610
54	5.565640668	5.585505668	5.606954704	5.629993780	5.654523686	5.679643610	5.705353610	5.731663610	5.758573610	5.786083610	5.814193610
55	5.578250668	5.598115668	5.620564704	5.644603780	5.670133686	5.696253610	5.722963610	5.750273610	5.778183610	5.806693610	5.835803610
56	5.590860668	5.610725668	5.634174704	5.659213780	5.685843686	5.713063610	5.740873610	5.769283610	5.798293610	5.827903610	5.858113610
57	5.603470668	5.623335668	5.646784704	5.672823780	5.700453686	5.729673610	5.760483610	5.792893610	5.826903610	5.862513610	5.898723610
58	5.616080668	5.635945668	5.659394704	5.685433780	5.713063686	5.742283610	5.773093610	5.805503610	5.839513610	5.875123610	5.911333610
59	5.628690668	5.648555668	5.671904704	5.697943780	5.726573686	5.756793610	5.788603610	5.822013610	5.857023610	5.893733610	5.931143610
60	5.641300668	5.661165668	5.684514704	5.710553780	5.739183686	5.769403610	5.801213610	5.834623610	5.869633610	5.906343610	5.943753610
61	5.653910668	5.673775668	5.697124704	5.723163780	5.751793686	5.782013610	5.813823610	5.847233610	5.882243610	5.918953610	5.956363610
62	5.666520668	5.686385668	5.709734704	5.735773780	5.764403686	5.794623610	5.826433610	5.859843610	5.894853610	5.931563610	5.968973610
63	5.679130668	5.698995668	5.722344704	5.748383780	5.777013686	5.807233610	5.839043610	5.872453610	5.907463610	5.944173610	5.981583610
64	5.691740668	5.711605668	5.734954704	5.760993780	5.790623686	5.821843610	5.854653610	5.889063610	5.925073610	5.962683610	5.999993610
65	5.704350668	5.724215668	5.747564704	5.773603780	5.803233686	5.835453610	5.869263610	5.904673610	5.941683610	5.979293610	6.017503610
66	5.716960668	5.736825668	5.759174704	5.785213780	5.814843686	5.847063610	5.880873610	5.916283610	5.953293610	5.990903610	6.029113610
67	5.729570668	5.749435668	5.771784704	5.797823780	5.827453686	5.859673610	5.893483610	5.928893610	5.965903610	6.003513610	6.041723610
68	5.742180668	5.762045668	5.784394704	5.810433780	5.839063686	5.871283610	5.906093610	5.942503610	5.980513610	6.019123610	6.058333610
69	5.754790668	5.774655668	5.796904704	5.822943780	5.852573686	5.884793610	5.919603610	5.956013610	5.994023610	6.032633610	6.071843610
70	5.767400668	5.787265668	5.809614704	5.835653780	5.865283686	5.897503610	5.932313610	5.968723610	6.006733610	6.045343610	6.084553610
71	5.779990668	5.799855668	5.822204704	5.848243780	5.877873686	5.910093610	5.944903610	5.981313610	6.019323610	6.057933610	6.097143610
72	5.792600668	5.812465668	5.834814704	5.860853780	5.890483686	5.922703610	5.957513610	5.993923610	6.031933610	6.070543610	6.109753610
73	5.805210668	5.825075668	5.847424704	5.873463780	5.903093686	5.935313610	5.970123610	6.006533610	6.044543610	6.083153610	6.122363610
74	5.817820668	5.837685668	5.859934704	5.885973780	5.915603686	5.947823610	5.982633610	6.019043610	6.057053610	6.095663610	6.134873610
75	5.830430668	5.850295668	5.872644704	5.898683780	5.928313686	5.960533610	5.995343610	6.031753610	6.069763610	6.108373610	6.147583610
76	5.843040668	5.862905668	5.885254704	5.911293780	5.940923686	5.973143610	6.007953610	6.044363610	6.082373610	6.120983610	6.159793610
77	5.855650668	5.875515668	5.897864704	5.923903780	5.953533686	5.985753610	6.020563610	6.056973610	6.094983610	6.133593610	6.172803610
78	5.868260668	5.888125668	5.910474704	5.936513780	5.966143686	5.998363610	6.033173610	6.069583610	6.107593610	6.146203610	6.185413610
79	5.880870668	5.900735668	5.923084704	5.949123780	5.978753686	6.010973610	6.045783610	6.082193610	6.119203610	6.156813610	6.195023610
80	5.893480668	5.913345668	5.935694704	5.961733780	5.991363686	6.023583610	6.058393610	6.094803610	6.132813610	6.171423610	6.210633610
81	5.906090668	5.925955668	5.948304704	5.974343780	6.003973686	6.036193610	6.071003610	6.107413610	6.145423610	6.184033610	6.223243610
82	5.918700668	5.938565668	5.960914704	5.986953780	6.016583686	6.048803610	6.083613610	6.120023610	6.158033610	6.196643610	6.235853610
83	5.931310668	5.951175668	5.973524704	6.000563780	6.029193686	6.061413610	6.096223610	6.133633610	6.172643610	6.212253610	6.252463610
84	5.943920668	5.963785668	5.986134704	6.012173780	6.041803686	6.074023610	6.108833610	6.146243610	6.185253610	6.224863610	6.265073610
85	5.956530668	5.976395668	5.998744704	6.024783780	6.054413686	6.086633610	6.121443610	6.158853610	6.197863610	6.237473610	6.277683610
86	5.969140668	5.989005668	6.011354704	6.037393780	6.067023686	6.099243610	6.134053610	6.172063610	6.211273610	6.251683610	6.292293610
87	5.981750668	5.999615668	6.021964704	6.047903780	6.077533686	6.109753610	6.143563610	6.180973610	6.220983610	6.262593610	6.304903610
88	5.994360668	6.012225668	6.034574704	6.060513780	6.089143686	6.121363610	6.156173610	6.194183610	6.234393610	6.275803610	6.318413610
89	6.006970668	6.024835668	6.047184704	6.073123780	6.101753686	6.133973610	6.168783610	6.206793610	6.247903610	6.291213610	6.335723610
90	6.019580668	6.037445668	6.059794704	6.085733780	6.114363686	6.146583610	6.181393610	6.219403610	6.260513610	6.303823610	6.348333610
91	6.032190668	6.050055668	6.072404704	6.098343780	6.126973686	6.159193610	6.193003610	6.229413610	6.268423610	6.309533610	6.352843610
92	6.044800668	6.062665668	6.085014704	6.110953780	6.139583686	6.171803610	6.206613610	6.244623610	6.285733610	6.329043610	6.373553610
93	6.057410668	6.075275668	6.097624704	6.123563780	6.152193686	6.184413610	6.219223610	6.257233610	6.298343610	6.341653610	6.386163610
94	6.070020668	6.087885668	6.110234704	6.136173780	6.164803686	6.197023610	6.231833610	6.269843610	6.310953610	6.355263610	6.401773610
95	6.082630668	6.100495668	6.122844704	6.148783780	6.177413686	6.209633610	6.243443610	6.280453610	6.320563610	6.363873610	6.409383610
96	6.095240668	6.113105668	6.135454704	6.161393780	6.190023686	6.222243610	6.256053610	6.293063610	6.333173610	6.376483610	6.422993610
97	6.107850668	6.125715668	6.148064704	6.174003780	6.202633686	6.234853610	6.268663610	6.305673610	6.345783610	6.389093610	6.434603610
98	6.120460668	6.138325668	6.160674704	6.186613780	6.215243686	6.247463610	6.281273610	6.318283610	6.358393610	6.401703610	6.447213610
99	6.133070668	6.150935668	6.173284704	6.199223780	6.227853686	6.259073610	6.292883610	6.330893610	6.371003610	6.414313610	6.460823610
100	6.145680668	6.163545668	6.185894704	6.211833780	6.240463686	6.271683610	6.305493610	6.342503610	6.382613610	6.425923610	6.472433610

q	0	1	2	3	4	5	6	7	8	9	10
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102	43, 4315156281	43, 4071932817	43, 4071932817	43, 4315156281	43, 604940469	43, 8517414598	44, 1415821857	44, 2209176304	44, 35070318	44, 5295732	45, 966566614
103	43, 3714448767	43, 3714448767	43, 3714448767	43, 3714448767	43, 3714448767	43, 851378660	44, 1117319757	44, 1695894135	44, 2938043761	44, 452233872	44, 801261519
104	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 793481204	44, 1117319759	44, 1695894135	44, 2938043761	44, 452233872	44, 801261519
105	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 793481204	44, 1117319759	44, 1695894135	44, 2938043761	44, 452233872	44, 801261519
106	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 793481204	44, 1117319759	44, 1695894135	44, 2938043761	44, 452233872	44, 801261519
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108	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 793481204	44, 1117319759	44, 1695894135	44, 2938043761	44, 452233872	44, 801261519
109	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 793481204	44, 1117319759	44, 1695894135	44, 2938043761	44, 452233872	44, 801261519
110	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 793481204	44, 1117319759	44, 1695894135	44, 2938043761	44, 452233872	44, 801261519
111	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 793481204	44, 1117319759	44, 1695894135	44, 2938043761	44, 452233872	44, 801261519
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128	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 793481204	44, 1117319759	44, 1695894135	44, 2938043761	44, 452233872	44, 801261519
129	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 3392595716	43, 793481204	44, 1117319759	44, 1695894135	44, 2938043761	44, 452233872	44, 801261519
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q	n	1	2	3	5	6	7	8	9	10
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152	42	116-854701	42	1256-771597	42	1586-622509	42	1954-442088	42	2598-911770
153	42	110-651794	42	1207-717149	42	1527-622509	42	1954-442088	42	2598-911770
154	42	108-627617	42	1180-717149	42	1507-622509	42	1954-442088	42	2598-911770
155	42	106-603540	42	1152-717149	42	1487-622509	42	1954-442088	42	2598-911770
156	42	104-579463	42	1124-717149	42	1467-622509	42	1954-442088	42	2598-911770
157	42	102-555386	42	1096-717149	42	1447-622509	42	1954-442088	42	2598-911770
158	42	100-531309	42	1068-717149	42	1427-622509	42	1954-442088	42	2598-911770
159	42	97-507232	42	1040-717149	42	1407-622509	42	1954-442088	42	2598-911770
160	42	95-483155	42	1012-717149	42	1387-622509	42	1954-442088	42	2598-911770
161	42	93-459078	42	984-717149	42	1367-622509	42	1954-442088	42	2598-911770
162	42	91-435001	42	956-717149	42	1347-622509	42	1954-442088	42	2598-911770
163	42	89-410924	42	928-717149	42	1327-622509	42	1954-442088	42	2598-911770
164	42	87-386847	42	900-717149	42	1307-622509	42	1954-442088	42	2598-911770
165	42	85-362770	42	872-717149	42	1287-622509	42	1954-442088	42	2598-911770
166	42	83-338693	42	844-717149	42	1267-622509	42	1954-442088	42	2598-911770
167	42	81-314616	42	816-717149	42	1247-622509	42	1954-442088	42	2598-911770
168	42	79-290539	42	788-717149	42	1227-622509	42	1954-442088	42	2598-911770
169	42	77-266462	42	760-717149	42	1207-622509	42	1954-442088	42	2598-911770
170	42	75-242385	42	732-717149	42	1187-622509	42	1954-442088	42	2598-911770
171	42	73-218308	42	704-717149	42	1167-622509	42	1954-442088	42	2598-911770
172	42	71-194231	42	676-717149	42	1147-622509	42	1954-442088	42	2598-911770
173	42	69-170154	42	648-717149	42	1127-622509	42	1954-442088	42	2598-911770
174	42	67-146077	42	620-717149	42	1107-622509	42	1954-442088	42	2598-911770
175	42	65-122000	42	592-717149	42	1087-622509	42	1954-442088	42	2598-911770
176	42	63-97823	42	564-717149	42	1067-622509	42	1954-442088	42	2598-911770
177	42	61-75426	42	536-717149	42	1047-622509	42	1954-442088	42	2598-911770
178	42	59-53049	42	508-717149	42	1027-622509	42	1954-442088	42	2598-911770
179	42	57-30652	42	480-717149	42	1007-622509	42	1954-442088	42	2598-911770
180	42	55-80845	42	452-717149	42	987-622509	42	1954-442088	42	2598-911770
181	42	53-58448	42	424-717149	42	967-622509	42	1954-442088	42	2598-911770
182	42	51-36051	42	396-717149	42	947-622509	42	1954-442088	42	2598-9117

$$K_{(n+1/2)} \left(\frac{1}{2} \sqrt{q} \right)$$

q	n	1	2	3	4	5	6	7	8	9	10
201	50	50.00456204	40.682212684	40.736683166	40.876237353	41.1090100763	41.1314468828	41.15686664	41.2705559035	41.3901402936	41.610276938
202	51	51.984944848	40.694953618	40.695460557	40.827444367	41.1306202131	41.13375374	41.1543358	41.28159573	41.39562579	41.610276938
203	52	52.969292207	40.707653636	40.708160575	40.840144187	41.139826235	41.14305977	41.164680951	41.292046695	41.406131905	41.610276938
204	53	53.953639571	40.720362654	40.720869593	40.852852266	41.149028759	41.15226230	41.173883474	41.301249218	41.415325428	41.610276938
205	54	54.937986925	40.733071672	40.733578611	40.859851345	41.158217783	41.161451324	41.183072498	41.310438242	41.424613852	41.610276938
206	55	55.922334279	40.745780690	40.746287629	40.872553374	41.167406803	41.170640344	41.192261518	41.323627262	41.433905362	41.610276938
207	56	56.906681633	40.758489708	40.758996647	40.885263393	41.176596283	41.179829824	41.201450998	41.336816352	41.443196872	41.610276938
208	57	57.891028987	40.771198726	40.771705665	40.897973399	41.185791763	41.189025304	41.210646478	41.349727342	41.452488382	41.610276938
209	58	58.875376341	40.783907744	40.784414683	40.910683387	41.194986743	41.198220284	41.219841458	41.362638322	41.461779892	41.610276938
210	59	59.859723695	40.796616762	40.797123701	40.923392461	41.204181723	41.207415264	41.229036438	41.375549302	41.471071402	41.610276938
211	60	60.844071049	40.809325780	40.809832719	40.936099539	41.213377003	41.216610544	41.238231718	41.388460282	41.480322912	41.610276938
212	61	61.828418403	40.822034800	40.822541739	40.948808559	41.222572283	41.225805824	41.247426998	41.397647962	41.489179522	41.610276938
213	62	62.812765757	40.834743818	40.835250757	40.961517577	41.231767563	41.235001104	41.256622278	41.406843242	41.498004802	41.610276938
214	63	63.797113111	40.847452836	40.847959775	40.974226595	41.240962843	41.244196384	41.265817558	41.416038202	41.507199762	41.610276938
215	64	64.781460465	40.860161854	40.860668793	40.986935613	41.250168523	41.253402064	41.275023238	41.425219162	41.516380722	41.610276938
216	65	65.765807819	40.872870872	40.873377811	40.999647591	41.259374203	41.262607744	41.284228918	41.434410082	41.525581282	41.610276938
217	66	66.750155173	40.885579890	40.886086829	40.999647591	41.268579883	41.271813424	41.293434598	41.443611102	41.534782302	41.610276938
218	67	67.734502527	40.898288908	40.898795847	40.999647591	41.277785563	41.281019104	41.302640278	41.452812122	41.543983322	41.610276938
219	68	68.718849881	40.911000000	40.911506939	40.999647591	41.286991243	41.290224784	41.311845958	41.462013142	41.554184342	41.610276938
220	69	69.703197235	40.923709090	40.924216029	40.999647591	41.296196923	41.299430464	41.321051638	41.471214162	41.564385362	41.610276938
221	70	70.687544589	40.936418181	40.936925120	40.999647591	41.305402603	41.308636144	41.330257318	41.480415182	41.573586382	41.610276938
222	71	71.671891943	40.949127272	40.949634211	40.999647591	41.314608243	41.317841784	41.339462958	41.489616202	41.582787402	41.610276938
223	72	72.656239297	40.961836363	40.962343302	40.999647591	41.323813883	41.327047424	41.348668598	41.498817242	41.591988442	41.610276938
224	73	73.640586651	40.974545454	40.975052393	40.999647591	41.333019023	41.336252564	41.357873738	41.508018282	41.601089482	41.610276938
225	74	74.624934005	40.987254545	40.987761484	40.999647591	41.342224163	41.345457704	41.367078878	41.517219322	41.612190522	41.610276938
226	75	75.609281359	40.999963636	40.999963636	40.999647591	41.351429303	41.354662844	41.376284018	41.526360362	41.623291562	41.610276938
227	76	76.593628713	41.012672727	41.013179666	40.999647591	41.360634443	41.363867984	41.385489158	41.536460802	41.634392602	41.610276938
228	77	77.577976067	41.025381818	41.025888757	40.999647591	41.369839583	41.373073124	41.394694298	41.546561842	41.645493642	41.610276938
229	78	78.562323421	41.038090909	41.038597848	40.999647591	41.379044723	41.382278264	41.403899438	41.556662882	41.656594682	41.610276938
230	79	79.546670775	41.050799999	41.051306938	40.999647591	41.388249863	41.391483404	41.413104578	41.566763922	41.667695722	41.610276938
231	80	80.531018129	41.063509090	41.064016029	40.999647591	41.397455003	41.400688544	41.422309718	41.576864962	41.678796762	41.610276938
232	81	81.515365483	41.076218181	41.076725120	40.999647591	41.406660143	41.409893684	41.431514858	41.586966002	41.689897802	41.610276938
233	82	82.500012837	41.088927272	41.089434211	40.999647591	41.415865283	41.419098824	41.440719998	41.597067042	41.700008842	41.610276938
234	83	83.484660191	41.101636363	41.102143302	40.999647591	41.425070423	41.428303964	41.449925138	41.607168082	41.711110882	41.610276938
235	84	84.469307545	41.114345454	41.114852393	40.999647591	41.434275563	41.437509104	41.459130278	41.617269122	41.722211882	41.610276938
236	85	85.453954899	41.127054545	41.127561484	40.999647591	41.443480703	41.446714244	41.468335418	41.627370162	41.733312922	41.610276938
237	86	86.438602253	41.139763636	41.140270575	40.999647591	41.452685843	41.455919384	41.477540558	41.637471202	41.744413962	41.610276938
238	87	87.423249607	41.152472727	41.152979666	40.999647591	41.461890983	41.465124524	41.486745698	41.647572242	41.755515002	41.610276938
239	88	88.407896961	41.165181818	41.165688757	40.999647591	41.471096123	41.474329664	41.495950838	41.657673282	41.766616042	41.610276938
240	89	89.392544315	41.177890909	41.178397848	40.999647591	41.480301263	41.483534804	41.505155978	41.667774322	41.777717082	41.610276938
241	90	90.377191669	41.190599999	41.191106938	40.999647591	41.489506403	41.492739944	41.514361118	41.677875362	41.788818122	41.610276938
242	91	91.361839023	41.203309090	41.203816029	40.999647591	41.498711543	41.501945084	41.523566258	41.687976402	41.799919162	41.610276938
243	92	92.346486377	41.216018181	41.216525120	40.999647591	41.507916683	41.511150224	41.532771398	41.698077442	41.810020202	41.610276938
244	93	93.331133731	41.228727272	41.229234211	40.999647591	41.517121823	41.520355364	41.541976538	41.708178482	41.821121242	41.610276938
245	94	94.315781085	41.241436363	41.241943302	40.999647591	41.526326963	41.529560504	41.551181678	41.718279522	41.832222282	41.610276938
246	95	95.300428439	41.254145454	41.254652393	40.999647591	41.535532103	41.538765644	41.560386818	41.728380562	41.843323322	41.610276938
247	96	96.285075793	41.266854545	41.267361484	40.999647591	41.544737243	41.547970784	41.569591958	41.738481602	41.854424362	41.610276938
248	97	97.269723147	41.279563636	41.280070575	40.999647591	41.553942383	41.557175924	41.578797098	41.748582642	41.865525402	41.610276938
249	98	98.254370501	41.292272727	41.292779666	40.999647591	41.563147523	41.566381064	41.587992238	41.758683682	41.876626442	41.610276938
250	99	99.239017855	41.304981818	41.305488757	40.999647591	41.572352663	41.575586204	41.597207378	41.768784722	41.887727482	41.610276938

n	0	1	2	3	4	5	6	7	8	9	10
0	50.840238108	51.383673849	52.924362672	54.461687140	55.961687140	57.4468690330	58.914272101	60.369475516	61.814272101	63.249516767	64.669516767
1	50.842978731	51.386553590	52.930235350	54.4639791542	55.964295591	57.449159540	58.916727516	60.372025216	61.816727516	63.252025216	64.672025216
2	50.845719153	51.389293918	52.932975678	54.466719476	55.966995916	57.451899540	58.919467516	60.374534960	61.819467516	63.254534960	64.674534960
3	50.848459575	51.392034340	52.935716000	54.469459898	55.969736242	57.454639930	58.922207930	60.377044704	61.822207930	63.257044704	64.677044704
4	50.851200000	51.394774762	52.938456322	54.472200320	55.972476568	57.457380354	58.924948354	60.379554448	61.824948354	63.259554448	64.679554448
5	50.853940422	51.397515184	52.941196644	54.474940742	55.975217006	57.460120778	58.927688778	60.382064192	61.827688778	63.262064192	64.682064192
6	50.856680844	51.400255606	52.943936966	54.477681164	55.977957444	57.462861200	58.930429200	60.384573936	61.830429200	63.264573936	64.684573936
7	50.859421266	51.402996028	52.946677288	54.480421586	55.980697870	57.465601622	58.933169622	60.387083680	61.833169622	63.267083680	64.687083680
8	50.862161688	51.405736450	52.949417610	54.483162008	55.983438292	57.468342044	58.935910044	60.389593424	61.835910044	63.269593424	64.689593424
9	50.864902110	51.408476872	52.952157932	54.485902430	55.986178714	57.471082466	58.938650466	60.392103168	61.838650466	63.272103168	64.692103168
10	50.867642532	51.411217294	52.954898254	54.488642852	55.988919136	57.473822888	58.941390888	60.394612912	61.841390888	63.274612912	64.694612912
11	50.870382954	51.413957716	52.957638576	54.491383274	55.991659558	57.476563310	58.944131310	60.397122656	61.844131310	63.277122656	64.697122656
12	50.873123376	51.416698138	52.960378898	54.494123696	55.994400000	57.479303732	58.946871732	60.399632400	61.846871732	63.279632400	64.700000000
13	50.875863798	51.419438560	52.963119220	54.496864118	55.997140422	57.482044154	58.949612154	60.402142144	61.849612154	63.282142144	64.702500000
14	50.878604220	51.422178982	52.965859542	54.499604540	55.999880844	57.484784576	58.952352576	60.404651888	61.852352576	63.284651888	64.705000000
15	50.881344642	51.424919404	52.968600000	54.502344962	56.002621266	57.487525000	58.955093000	60.407161632	61.855093000	63.287161632	64.707500000
16	50.884085064	51.427659826	52.971340322	54.505085384	56.005361688	57.490265422	58.957833422	60.409671376	61.857833422	63.289671376	64.710000000
17	50.886825486	51.430400248	52.974080644	54.507825806	56.008102110	57.493005844	58.960573844	60.412181120	61.860573844	63.292181120	64.712500000
18	50.889565908	51.433140670	52.976820966	54.510566228	56.010842532	57.495746266	58.963314266	60.414690864	61.863314266	63.294690864	64.715000000
19	50.892306330	51.435881092	52.979561288	54.513306650	56.013582954	57.498486688	58.966054688	60.417200608	61.866054688	63.297200608	64.717500000
20	50.895046752	51.438621514	52.982301710	54.516047072	56.016323376	57.501227110	58.968795110	60.419710352	61.868795110	63.299710352	64.720000000
21	50.897787174	51.441361936	52.985042132	54.518787494	56.019063798	57.503967532	58.971535532	60.422220096	61.871535532	63.302220096	64.722500000
22	50.900527596	51.444102358	52.987782554	54.521527916	56.021804220	57.506707954	58.974275954	60.424729840	61.874275954	63.304729840	64.725000000
23	50.903268018	51.446842780	52.990522976	54.524268338	56.024544642	57.509448376	58.977016376	60.427239584	61.877016376	63.307239584	64.727500000
24	50.906008440	51.449583202	52.993263398	54.527008760	56.027285064	57.512188798	58.979756798	60.429749328	61.879756798	63.309749328	64.730000000
25	50.908748862	51.452323624	52.996003820	54.529749182	56.030025486	57.514929220	58.982497220	60.432259072	61.882497220	63.312259072	64.732500000
26	50.911489284	51.455064046	52.998744242	54.532489604	56.032765908	57.517669642	58.985237642	60.434768816	61.885237642	63.314768816	64.735000000
27	50.914229706	51.457804468	52.999984664	54.535230026	56.035506330	57.520410064	58.987978064	60.437278560	61.887978064	63.317278560	64.737500000
28	50.916970128	51.460544890	53.000225086	54.537970448	56.038246752	57.523150486	58.990718486	60.439788304	61.890718486	63.319788304	64.740000000
29	50.919710550	51.463285312	53.000465508	54.540710870	56.040987174	57.525890908	58.993458908	60.442298048	61.893458908	63.322298048	64.742500000
30	50.922450972	51.466025734	53.000705930	54.543451292	56.043727596	57.528631330	58.996199330	60.444807792	61.896199330	63.324807792	64.745000000
31	50.925191394	51.468766156	53.000946352	54.546191714	56.046468018	57.531371752	58.998939752	60.447317536	61.898939752	63.327317536	64.747500000
32	50.927931816	51.471506578	53.001186774	54.548932136	56.049208440	57.534112174	59.001680174	60.449827280	61.901680174	63.329827280	64.750000000
33	50.930672238	51.474246999	53.001427196	54.551672558	56.051948862	57.536852596	59.004420596	60.452337024	61.904420596	63.332337024	64.752500000
34	50.933412660	51.476987421	53.001667618	54.554412980	56.054689284	57.539593018	59.007161018	60.454846768	61.907161018	63.334846768	64.755000000
35	50.936153082	51.479727843	53.001908040	54.557153402	56.057429706	57.542333440	59.009901440	60.457356512	61.909901440	63.337356512	64.757500000
36	50.938893504	51.482468265	53.002148462	54.559893824	56.060170128	57.545073862	59.012641862	60.459866256	61.912641862	63.339866256	64.760000000
37	50.941633926	51.485208687	53.002388884	54.562634246	56.062910550	57.547814284	59.015382284	60.462376000	61.915382284	63.342376000	64.762500000
38	50.944374348	51.487949109	53.002629306	54.565374668	56.065650972	57.550554706	59.018122706	60.464885744	61.918122706	63.344885744	64.765000000
39	50.947114770	51.490689531	53.002869728	54.568115090	56.068391394	57.553295128	59.020863128	60.467395488	61.920863128	63.347395488	64.767500000
40	50.949855192	51.493429953	53.003110150	54.570855512	56.071131816	57.556035550	59.023603550	60.469905232	61.923603550	63.349905232	64.770000000
41	50.952595614	51.496170375	53.003350572	54.573595934	56.073872238	57.558775972	59.026343972	60.472414976	61.926343972	63.352414976	64.772500000
42	50.955336036	51.498910797	53.003590994	54.576336356	56.076612660	57.561516394	59.029084394	60.474924720	61.929084394	63.354924720	64.775000000
43	50.958076458	51.501651219	53.003831416	54.579076778	56.079353082	57.564256816	59.031824816	60.477434464	61.931824816	63.357434464	64.777500000
44	50.960816880	51.504391641	53.004071838	54.581817200	56.082093504	57.567000000	59.034565238	60.479944208	61.934565238	63.359944208	64.780000000
45	50.963557302	51.507132063	53.004312260	54.584557622	56.084833926	57.569740422	59.037305660	60.482453952	61.937305660	63.362453952	64.782500000
46	50.966297724	51.509872485	53.004552682	54.587298044	56.087574348	57.572480844	59.040046082	60.484963696	61.940046082	63.364963696	64.785000000
47	50.969038146	51.512612907	53.004793104	54.590038466	56.090314770	57.575221266	59.042786504	60.487473440	61.942786504	63.367473440	64.787500000
48	50.971778568	51.515353329	53.005033526	54.592778888	56.093055192	57.577961688	59.045526926	60.489983184	61.945526926	63.369983184	64.790000000
49	50.974518990	51.518093751	53.005273948	54.595519310	56.095795614	57.580702110	59.048267348	60.492492928	61.948267348	63.372492928	64.792500000
50	50.977259412	51.520834173	53.005514370	54.598259732	56.098536036	57.583442532	59.051007770	60.495002672	61.951007770	63.375002672	64.795000000

$$K(n + \frac{1}{2})(\sqrt[3]{\sqrt{q}})$$

q	0	1	2	3	4	5	6	7	8	9	10
101	46.103851363	46.1162517977	46.1286517977	46.1410517977	46.1534517977	46.1658517977	46.1782517977	46.1906517977	46.2030517977	46.2154517977	46.2278517977
102	46.1076317670	46.1199317670	46.1322317670	46.1445317670	46.1568317670	46.1691317670	46.1814317670	46.1937317670	46.2060317670	46.2183317670	46.2306317670
103	46.1114117670	46.1237117670	46.1360117670	46.1483117670	46.1606117670	46.1729117670	46.1852117670	46.1975117670	46.2098117670	46.2221117670	46.2344117670
104	46.1151917670	46.1274917670	46.1397917670	46.1520917670	46.1643917670	46.1766917670	46.1889917670	46.2012917670	46.2135917670	46.2258917670	46.2381917670
105	46.1189717670	46.1312717670	46.1435717670	46.1558717670	46.1681717670	46.1804717670	46.1927717670	46.2050717670	46.2173717670	46.2296717670	46.2419717670
106	46.1227517670	46.1350517670	46.1473517670	46.1596517670	46.1719517670	46.1842517670	46.1965517670	46.2088517670	46.2211517670	46.2334517670	46.2457517670
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109	46.1340917670	46.1463917670	46.1586917670	46.1709917670	46.1832917670	46.1955917670	46.2078917670	46.2201917670	46.2324917670	46.2447917670	46.2570917670
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113	46.1492117670	46.1615117670	46.1738117670	46.1861117670	46.1984117670	46.2107117670	46.2230117670	46.2353117670	46.2476117670	46.2599117670	46.2722117670
114	46.1529917670	46.1652917670	46.1775917670	46.1898917670	46.2021917670	46.2144917670	46.2267917670	46.2390917670	46.2513917670	46.2636917670	46.2759917670
115	46.1567717670	46.1690717670	46.1813717670	46.1936717670	46.2059717670	46.2182717670	46.2305717670	46.2428717670	46.2551717670	46.2674717670	46.2797717670
116	46.1605517670	46.1728517670	46.1851517670	46.1974517670	46.2097517670	46.2220517670	46.2343517670	46.2466517670	46.2589517670	46.2712517670	46.2835517670
117	46.1643317670	46.1766317670	46.1889317670	46.2012317670	46.2135317670	46.2258317670	46.2381317670	46.2504317670	46.2627317670	46.2750317670	46.2873317670
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[illegible]

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In general, for a given argument, this formula was used to calculate two of the functions, with orders differing by unity, and the recursion formula

$$(3) \quad K_{n+1}(z) = K_{n-1}(z) + \frac{2n}{z} K_n(z)$$

was then used to compute the other orders required.

For half-integral orders, the series in equation (2) is exact, and no difficulty arose in the calculation of the corresponding tables. For integral orders the terms of the series eventually diverge; and in order to cope with this, three separate ranges of the argument were considered as follows:

(i) $z \geq 10$

In this range the computer calculated $K_0(z)$ and $K_1(z)$ and built up the other orders using equation (3). The asymptotic series was summed up to the point where the terms began to diverge, and the series was then rounded off by adding to the sum one half of the first divergent term. Within its range this approximation gave almost 12-figure accuracy in the results.

(ii) $3.6 \leq z < 10$

Over this range a method due to Dingle (1958a, 1959) was employed to calculate a more accurate converging factor than the crude value 0.5 used in the first range of z . Generally, in this method, the asymptotic series is allowed to run on for a number of terms beyond the first divergent one, and is cut off after p terms, where p depends upon the values of n and z in $K_n(z)$. The converging factor Σ_t , which is applied to the last term calculated, may be written

$$(4) \quad \Sigma_t = \sum_{l=0}^{\infty} \frac{\Gamma(n+\frac{1}{2})\Gamma(n+p+\frac{1}{2}-l)}{\Gamma(n+\frac{1}{2}-l)\Gamma(n+p+\frac{1}{2})} (-2z)^l \Lambda_{p-n-\frac{1}{2}}^{(l)}(2z)$$

where the $\Lambda_{p-n-\frac{1}{2}}^{(l)}$ are defined in the form

$$(5) \quad \Lambda_s^{(l)}(s+\theta) = \sum_{r=t}^{\infty} \sum_{q=0}^{r-t} a_{t,r} s^{-r} b_{t,r,q} \theta^q.$$

The numerical factors $a_{t,r}$ and $b_{t,r,q}$ are given by Dingle (1958b, 1959) up to terms in $t = 3$.^{*} Values of p and θ were found from the relationship

$$(6) \quad p - n - \frac{1}{2} = s$$

$$(7) \quad 2z = s + \theta$$

where in accordance with the derivation of equation (5), θ is restricted to small values; $|\theta| < 0.5$. Since p and n must be integers, s was chosen to be the half-integer nearest to $2z$; p was then obtained from equation (6). Because the series for the converging factor is itself asymptotic, it was necessary to insert into the computer program a test which was arranged to cut off Σ_t correctly at its least term. For this range of z , the best results were obtained by calculating $K_2(z)$ and $K_3(z)$ and using the recursion formula to obtain the

^{*}In the calculation of the tables, the expressions in equations (4) and (5) were used up to terms in $l = 4$ and a minor error in Dingle's expression for $\Lambda_1^{(1)}$ was corrected.

other orders. Above $z = 5$ the method gave results accurate to at least 11 figures; but from this point down to $z = 3.6$ the accuracy fell off steadily. In the region $z = 3.6$ –4.5 the error in the tables may amount to ± 1 unit in the 10th figure.

(iii) $0 < z < 3.6$

This is the only range in which a method independent of equation (2) was used to calculate the Bessel functions. The method is adequately described by Aldis (1899) and will not be repeated here; it makes use of series which occur in the calculation of the modified Bessel functions of the first kind. In this range $K_0(z)$ and $K_1(z)$ were calculated as a basis for the application of equation (3). The accuracy of the method is limited essentially by the fact that the two basic $K_n(z)$ are derived as the differences of other series each of which could only be calculated on the computer to a limited number of figures. Once again in the region of $z = 3.6$ the absolute value of the error in $K_n(z)$ may approach one unit in the 10th place; on going to lower values of z , however, the accuracy improves until, in the region of $z = 0.1$, 12-figure accuracy is obtained.

In order to estimate the limits of the various ranges of the argument, and to decide the magnitude of the errors within the ranges, sets of values of $K_0(z)$ and $K_1(z)$ were computed by the various methods described above, for values of z increasing by 0.1 in the range $0 < z \leq 6$, and by 1.0 in the range $6 \leq z \leq 12$; these were compared with a table of more accurate values of $K_0(z)$ and $K_1(z)$ over the same range, given by Aldis (1899). These computations served also to compare Dingle's method of calculating the converging factor for the asymptotic series with a simpler method due to Burnett (1930); this work forms the basis of a separate note (Dempsey and Benson, unpublished).

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REFERENCES

- ALDIS, W. S. 1899. *Proc. Roy. Soc. (London)*, A, **64**, 203.
 BENSON, G. C., BALK, P., and WHITE, P. 1959. *J. Chem. Phys.* **31**, 109.
 BENSON, G. C., DEMPSEY, E., and BALK, P. Unpublished.
 BURNETT, D. 1930. *Proc. Cambridge Phil. Soc.* **26**, 145.
 DEMPSEY, E. and BENSON, G. C. Unpublished.
 DINGLE, R. B. 1958a. *Proc. Roy. Soc. (London)*, A, **244**, 456.
 ——— 1958b. *Proc. Roy. Soc. (London)*, A, **244**, 476.
 ——— 1959. *Proc. Roy. Soc. (London)*, A, **249**, 270.
 DURHAM, G. S. and SODERBERG, B. A. 1958. *J. Chem. Phys.* **28**, 1201.
 HARTMAN, P. 1956. *Acta Cryst.* **9**, 569.
 VAN DER HOFF, B. M. E. and BENSON, G. C. 1953. *Can. J. Phys.* **31**, 1087.
 HOVE, J. and KRUMHANS, J. A. 1953. *Phys. Rev.* **92**, 569.
 LENNARD-JONES, J. E. and DENT, B. M. 1928. *Trans. Faraday Soc.* **24**, 92.
 MADELUNG, E. 1918. *Physik. Z.* **19**, 524.
 SCHREIBER, H. P. and BENSON, G. C. 1955. *Can. J. Phys.* **33**, 534.
 SHUTTLEWORTH, R. 1949. *Proc. Phys. Soc. (London)*, A, **62**, 167.
 WATSON, G. N. 1948. *A treatise on the theory of Bessel functions*, 2nd ed. (Cambridge University Press, London), p. 78.
 VAN ZEGGEREN, F. and BENSON, G. C. 1957. *J. Chem. Phys.* **26**, 1077.

AN ANALYSIS OF SOME STATISTICAL PROPERTIES OF AURORAL RADAR REFLECTIONS AND THEIR RELATIONSHIPS TO THE DETECTION CAPABILITIES OF THE RADAR¹

A. G. McNAMARA

ABSTRACT

A statistical model of auroral echo occurrence has been made from an analysis of observations at 48.5 Mc/s obtained over a number of years of continuous operation. The probability density distribution of auroral target cross sections (σ) has been examined experimentally, and the resulting curve fitted by simple mathematical relations. Both an inverse power law and an exponential law have been derived, of the forms

$$p(\sigma)d\sigma = k\sigma^{-1.67}d\sigma$$

and

$$p(\sigma)d\sigma = \frac{1}{\sigma_m} e^{-\sigma/\sigma_m} d\sigma.$$

These models have been interpreted in terms of distributed and localized targets, and used to analyze the echo occurrence indices and the effect which variation of radar parameters will have upon them. Both forms of the target law are useful although it is considered that the exponential form yields better agreement with observations over a wider range of the variables.

1. INTRODUCTION

A previous paper (McNamara 1958) has given the details of an auroral radar designed for continuous unattended monitoring of radar echoes from aurora. Two complementary forms of record are obtained from the radar and are scaled to give measures of echo occurrence. This paper examines the parameters involved in the design of equipment for auroral detection, and their relationship to the performance, echoes obtained, range distribution, scaling procedure, and indices derived from the data.

2. A RADAR EQUATION FOR AURORAL ECHOES

For the j th single elementary target, of small dimensions, the received power at time t_0 is given by (Kerr 1951)

$$(1) \quad P_{rj} = \frac{p(R_j)G_t G_r \lambda^2 F_t^2(\theta, \phi) F_r^2(\theta, \phi) A(\theta, \phi) \sigma_j}{64 \pi^3 R_j^4}$$

where t, r refer to the transmitting and receiving parameters respectively and

$p(R_j)$ = a function proportional to the magnitude of the Poynting vector of the incident wave at R at such time that the reflected signal from the scatterer returns to the receiver at the instant t_0 under consideration,

G = power gain of the antenna over an isotropic radiator,

λ = radio-frequency wavelength,

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- $F(\theta, \phi)$ = pattern propagation factor of the field strength,
 $\quad = f(\theta, \phi) \cdot g(\theta),$
 $f(\theta, \phi)$ = antenna pattern function expressing the relative free space field strength in the direction specified by elevation and azimuth angles θ and ϕ ,
 $g(\theta)$ = interference function, between the direct and ground-reflected rays, giving the field strength in the specified elevation relative to the maximum field strength in free space,
 σ_j = equivalent backscattering area of the elementary target,
 R = range to the target,
 $A_j(\theta, \phi)$ = the aspect function of the target cross section, giving the factor by which the effective target area is reduced when the target is located in the direction θ, ϕ .

From a consideration of the characteristics of auroral echoes, the actual targets are thought to be represented by a number of scatterers which scatter in a non-coherent manner relative to each other. The received power is the arithmetic sum of the powers from individual scatterers, and is averaged over a short period of time (the integration time of the eye, the camera viewing the cathode ray tube, or other recording device). Observations (Currie, Forsyth, and Vawter 1953; McNamara and Currie 1954; Unwin and Gadsden 1957) also indicate that the auroral echoing region is a relatively thin layer, over which the elementary targets will be considered to be distributed.

For non-isotropically scattering targets, the returned signal is modified by an 'aspect attenuation' function which is dependent upon the angle of incidence of the radiation on asymmetrical targets and hence upon the geometry of the radar case. The aspect function will be denoted by $A(\psi)$ where ψ is the angle of intersection with the major axis of the target, which is assumed to have axial symmetry about the earth's magnetic field, and by $A(\theta, \phi)$ relative to the radar. At a constant height of reflection, the aspect function can be expressed in terms of range and azimuth from the radar by the function $A(R, \phi)$, or along a specified beam direction by $A(R)$.

Radar observations at 50 Mc/s show that echoes can be received at angles deviating by as much as 15° from orthogonality to the magnetic field. Hence the length of field-aligned concentrations generally will not be greater than several tens of meters if such a beam width is to be observed in the scattering pattern of the target. This dimension is much less than a Fresnel zone and the range dependence of the scattered power from such elementary targets will still be as R^{-4} as in equation (1).

The horizontal distribution of targets may now be classified under the two conditions:

Case (i): The scattering region completely fills the azimuthal beam width.

Case (ii): The scattering region is more localized in space, occupying only a fraction of the azimuthal beam width.

In both cases the extent in range of the scattering region will be assumed to be appreciable, i.e., greater than the pulse lengths commonly employed.

The scatterers are considered independent and the received power, averaged over many pulse periods, is the sum of the average powers from each contributing scatterer.

For case (i), the density function $n(R, \phi, \bar{\sigma}) R dR d\phi d\bar{\sigma}$ is now introduced. This is the number of scatterers per unit area of cross section $\bar{\sigma}$ to $\bar{\sigma} + d\bar{\sigma}$. If the scatterers are uniformly distributed horizontally, then the density function separates in the integration yielding

$$\int_0^{\infty} \bar{\sigma} n(\bar{\sigma}) d\bar{\sigma} \equiv \sigma m^2 / m^2,$$

the average cross section per unit area of the ionosphere. Hence the signal-to-noise ratio is

$$(2) \quad \frac{P_r}{P_n} = \frac{G_t G_r \lambda^2 \sigma}{64 \pi^3 k T_e B} \int_0^{\infty} \int_{-\pi}^{\pi} F_t^2(\theta, \phi) F_r^2(\theta, \phi) A(\theta, \phi) d\phi \frac{p(R)}{R^3} dR.$$

Now a "beam width" Φ may be defined by

$$(3) \quad \int_{-\pi}^{\pi} F_t^2(\theta, \phi) F_r^2(\theta, \phi) A(\theta, \phi) d\phi = \Phi F_t^2(\theta, 0) F_r^2(\theta, 0) A(\theta, 0).$$

Within the next integral, $p(R)$ is non-zero only over a short interval roughly equivalent to the pulse length. Over this small interval the other factors in the integrand are substantially constant and may be moved outside the integral. There remains

$$(4) \quad \int_0^{\infty} p(R) dR = P_t \cdot \frac{\tau c}{2}$$

where the definition is in terms of the conventional values

P_t = peak power transmitted,

τ = pulse duration,

c = velocity of propagation of the electromagnetic energy.

Also

P_n = total noise power referred to the receiver input terminals,
 $= k T_e B,$

k = Boltzmann's constant,

T_e = effective absolute temperature of the source, including the effects of system noise, atmospheric noise, and cosmic noise,

B = noise bandwidth of the receiver.

Collecting all the parts

$$(5) \quad \frac{P_r}{P_n} = \frac{P_t G_t G_r \lambda^2}{64 \pi^3 k T_e B} \frac{\tau c}{2} \Phi \frac{F_t^2(\theta, 0) F_r^2(\theta, 0) A(\theta, 0)}{R^3} \sigma.$$

Turning now to case (ii) and starting with equation (1), the ensemble of scatterers may be replaced by equivalent scatterers of time and azimuthal average cross section $\sigma(m^2/m)$ located at the centers of the active region.

$$(6) \quad \frac{P_r}{P_n} = \frac{P_t G_t G_r \lambda^2}{64 \pi^3 k T_e B} \frac{\tau c}{2} \frac{F_t^2(\theta, \phi) F_r^2(\theta, \phi) A(\theta, \phi)}{R^4} \cdot \sigma.$$

Since we shall be interested in following the long-term variations of σ through P_r , we shall introduce the approximation that the propagation patterns and aspect factor are broad and flat in the azimuthal direction and cut off sharply beyond some critical azimuth. Then for a fixed broad beam radar, equation (6) reduces to the approximate form

$$(7) \quad \frac{P_r}{P_n} = \frac{P_t G_r \lambda^2 \tau c}{64 \pi^3 k T_e B} \frac{F_t^2(\theta, 0) F_r^2(\theta, 0) F(\theta, 0)}{R^4} \sigma.$$

This formulation will also be applicable to a rotating narrow beam.

Other factors being constant, it will be noted that the signal-to-noise ratio is proportional to $P_t \tau / B$ where the factor τ arises from spatial integration of the distributed target by the pulse length. For optimum signal-to-noise in the receiver, the bandwidth should be approximately equal to the inverse of the pulse length and the signal-to-noise ratio becomes proportional to $P_t \tau^2$. Hence peak power may be traded for narrow bandwidth and a large high-power radar may be replaced by a compact, reliable, low-power equipment. As an example, for a completely distributed target, a 1-kilowatt 300- μ sec pulse radar can approach the detection sensitivity of a 100-kilowatt 30- μ sec pulse radar.

For any given radar the received power sensitivity is determined by the antenna system through a fourth-degree propagation pattern. Since in practice all propagation patterns, both for horizontal and vertical polarization, have a null at zero degrees elevation, the detection of echoes at low elevation is sharply dependent on F and hence on antenna height. If antenna height is made too great, however, nulls in the pattern may appear at important echo elevations.

3. DEFINITIONS AND INDICES OF ECHO OCCURRENCE

The most complete and detailed description of echo occurrence conveniently obtainable from a range-time recording with a fixed beam radar is obtained by a method whereby the range-time record is searched in units which are one equivalent pulse length of range ($\tau c/2$) by one unit of time, and an occurrence is defined if an auroral echo is detectable in this cell. These can also be grouped under either the range intervals or time to obtain statistics on variation of occurrence with range or percentage time of occurrence of echoes respectively. The latter quantity, the occurrence of any auroral signal at any range in a unit time interval, is advantageous in that it applies uniformly to any equivalent pulse or continuous wave system and it is much more quickly read from the film record. Moreover, this index can also be obtained directly and immediately from the chart record produced by the signal integrator (McNamara 1958). The integrator also yields another index which is a measure of intensity of the disturbance. For daily measures the area under the trace of the time variation of signal amplitude, integrated over all ranges, may be scaled. On the daily basis, plots of the experimental data of percentage occurrence and integrated area, both derived from the integrator charts, show a fairly well-defined statistical relation between the two indices, although these indices, on occasion, may be expected to differ considerably. The relationship

is demonstrated in Fig. 1, where 423 daily points from the period 4 April 1956 to 31 May 1957 have been used. The data is well fitted by the parabola (solid line) of Fig. 1. The dashed lines give the values of the first-order standard deviations.

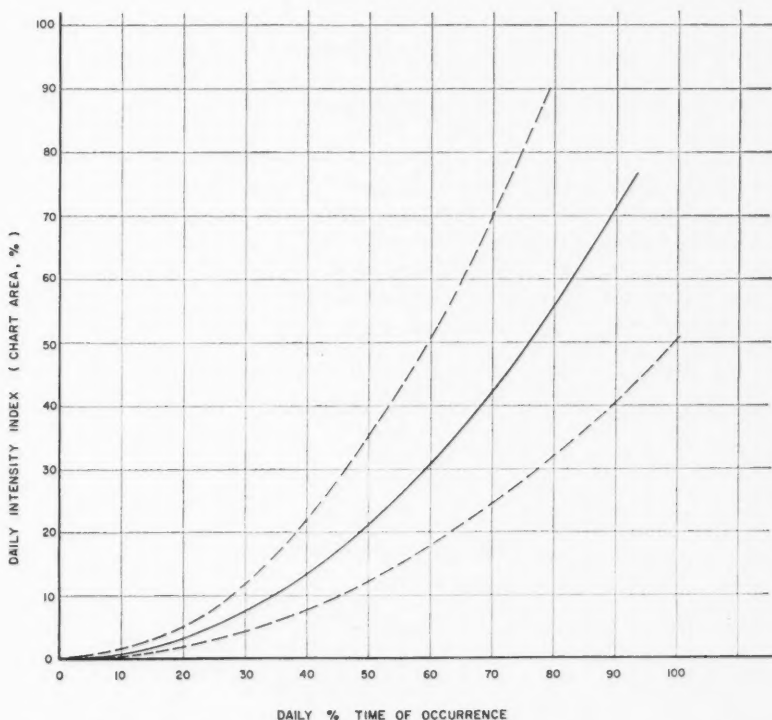


FIG. 1. The statistical relationship between 423 daily indices of echo intensity and duration of occurrence. The solid line is the line of best fit and the dashed lines are the first-order standard deviations.

4. DERIVATION OF ECHO OCCURRENCE FORMULAS

As discussed in Section 2, observations indicate that the auroral echoing region is a relatively thin layer over which we will consider the long-term unit-area target cross-section probability density function to be given by $p(\sigma)$ where $p(\sigma)$ is defined as

$$(8) \quad p(\sigma) = \frac{\text{(number of time units in which a target occurs with cross section between } \sigma \text{ and } \sigma + \Delta\sigma)}{\text{(total number of time units = } n)} \bigg/ \Delta\sigma$$

$$\Delta\sigma \rightarrow 0,$$

$$n \rightarrow \infty.$$

It will be implicitly assumed here that the probability density function is independent of the geographical position over the ionosphere. This is at least reasonable over the limited region viewed by a radar. Geographical variations in the frequency of occurrence are accounted for by a multiplicative factor $N(R, \phi)$, which represents the average rate of occurrence of all targets per unit area of the ionosphere. Therefore, the number of targets observable per unit area over an extended period of time is proportional to

$$(9) \quad N(R, \phi) \cdot \int_{\sigma_L}^{\infty} p(\sigma) d\sigma$$

where σ_L is the limiting cross section for threshold detection on the radar.

For the geometry of a thin auroral echoing layer at height h over a curved earth, it may be shown that the occurrence of targets in a range interval R_1 to R_2 is approximated closely for case (i) by

$$(10) \quad D = \int_{R_1}^{R_2} \int_{\sigma_L}^{\infty} \left(\frac{1 + (h/\rho)}{\cos \alpha} \right) N(R, \phi) p(\sigma) d\sigma dR \approx \int_{R_1}^{R_2} N(R, \phi) dR \int_{\sigma_L}^{\infty} p(\sigma) d\sigma$$

and for case (ii) by

$$(11) \quad D = \int_{R_1}^{R_2} \int_{\sigma_L}^{\infty} \left(\frac{1 + (h/\rho)}{\cos \alpha} \right) N(R, \phi) p(\sigma) R d\sigma dR \\ \approx \int_{R_1}^{R_2} N(R, \phi) R dR \int_{\sigma_L}^{\infty} p(\sigma) d\sigma$$

where ρ = radius of the earth,

α = angle subtended at the center of the earth by the arc from the radar to the subtarget point,

and $(h/\rho) \ll 1$, $\cos \alpha \approx 1$ for ranges at which echoes occur.

From this point onward, we shall only carry out the development of case (ii). Case (i) is then obtainable from any of the case (ii) equations by deleting the multiplicative R factor and by changing the R^{-4} to an R^{-3} .

The minimum detectable signal is taken to be a constant given by $P_{\tau_{\min}}/P_n = 1/b$. (In practice, a nominal threshold value of $b = 1$ is often used.)

From equation (7)

$$(12) \quad \frac{1}{\sigma_L} = \frac{b P_t G_r G_r \lambda^2}{k T_e B} \cdot \frac{F_i^2(\theta, 0) F_r^2(\theta, 0)}{64 \pi^3 R^4} \cdot \frac{\tau c}{2} \Phi_A(\theta, 0).$$

But

$$(13a) \quad \int_{\sigma_L}^{\infty} p(\sigma) d\sigma = f\{\sigma_L\} \text{ since the integral goes to zero at the upper limit}$$

$$(13b) \quad = f \left\{ \frac{1}{b} \cdot \frac{k T_e B}{P_t G_r G_r \lambda^2} \cdot \frac{64 \pi^3 R^4}{F_i^2(\theta, 0) F_r^2(\theta, 0)} \cdot \frac{2}{\tau c} \cdot \frac{1}{\Phi_A(\theta, 0)} \right\}$$

and therefore

$$(14) \quad D = \int_{R_1}^{R_2} f\{\sigma_L\} \cdot N(R, \phi) \cdot R \cdot dR.$$

To predict the range distribution, small range segments are taken. If the range segments are all equal and sufficiently small, then by the mean value theorem the range distribution D' is well represented by the integrand

$$(15) \quad D' = f\{\sigma_L\} \cdot N(R, \phi) \cdot R.$$

The term which is most uncertain is $f\{\sigma_L\}$ due to the aspect factor A contained within it. In principle it should be possible to plot the distribution D' by setting $A = 1$ and estimating values of N from other sources, and by using the difference between this curve and the observed range distribution to derive the aspect function A .

From radar observations, the aspect factor appears to be tolerant of small departures from normality but falls rapidly with increasing departures producing a rather sharp cutoff of echo occurrence at some minimum range. Theoretical derivations of an aspect function have been made by several authors on the bases of definite scattering models, and these could be substituted in the above relations. However, for determination of certain statistical properties of total echo occurrence no assumptions need be made of a physical model, and a simple linear approximation can be used to represent the attenuation. For illustrative purposes, A will be represented here by the ramp-like function

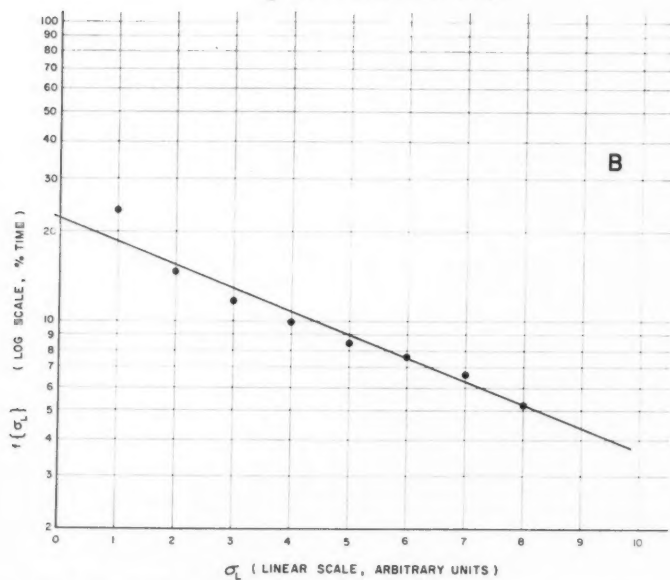
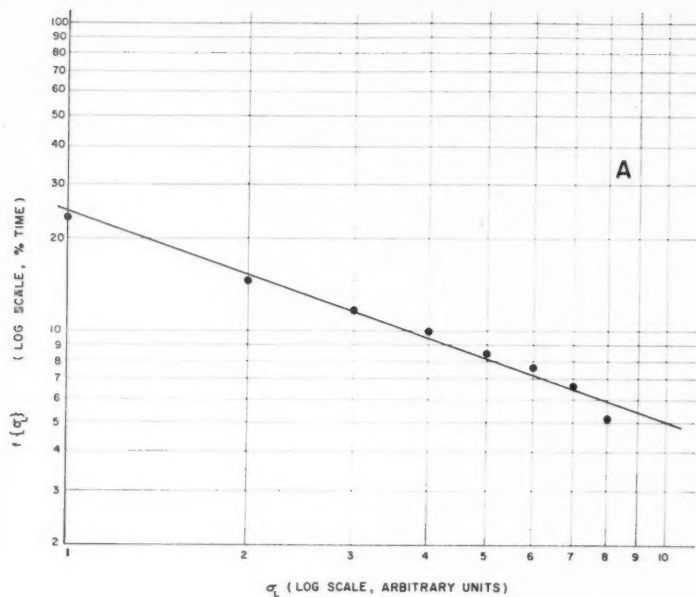
$$(16) \quad \begin{aligned} A(R) &= 0 & R < R_0, \\ &= \frac{R - R_0}{R_1 - R_0} & R_0 < R < R_1, \\ &= 1 & R > R_1. \end{aligned}$$

The cutoff range R_0 and the 'full-signal' range R_1 are suitably chosen with reference to the observed range distribution or by examination of the aspect angle ψ (for example, Figs. 4 or 3 of McNamara 1958). Although this results in inaccuracies in range distribution near the cutoff, the integral or total occurrence is not greatly in error if R_0 or R_1 are well selected.

The function $N(R)$ expressing the true geographical variation of mean auroral occurrence is not well established at present. It is necessary to know the zenithal occurrence at each point. Again, we shall make a simplification by setting $N(R) = 1$.

5. EXPERIMENTAL AND THEORETICAL PROBABILITY DENSITY FUNCTIONS FOR TARGET CROSS SECTIONS

The law which governs the distribution of target size is required to specify the nature of the function $f\{\sigma_L\}$ used in the preceding section. To this end, calibration of the over-all receiving-recording system was made with a random noise generator on the receiver input since this type of signal is most representative of auroral signals. The recording characteristic was thus established as nearly linear with noise power input, and hence linear with echo cross section σ . Echo data were derived from 469 days of consecutive operation, 1 January 1957 to 14 April 1958. The function scaled was actually the inte-



FIGS. 2A and 2B. Experimentally derived target cross-section distributions fitted to a power law (A) and to an exponential law (B); Fig. 2A yields the slope $m-1 = 0.68$ and Fig. 2B yields the mean cross section $\sigma_m = 5.3$.

grated probability density, $f\{\sigma_L\}$, defined by equation (13a). This was obtained by determining the time that the signal level was above a series of selected levels on the chart.

Mathematical description of the cross-section distribution was obtained by fitting simple expressions to the data. Figures 2A and 2B show the results of assuming an inverse power law and an exponential law. Reasonably good fits are obtained over the dynamic recording range for both forms. In the following the consequences of both approximations will be examined. Further discussion of the applicability of the laws will then be given.

(a) The inverse power law:

$$(17) \quad p(\sigma)d\sigma = \frac{K}{\sigma^m} d\sigma.$$

Hence

$$(18) \quad \int_{\sigma_L}^{\infty} p(\sigma)d\sigma = \frac{K'}{\sigma_L^{m-1}} \equiv f\{\sigma_L\} \quad \text{provided } m > 1$$

and

$$(19a) \quad D' = \left\{ \frac{K'}{(\sigma_L)^{m-1}} \right\} \cdot R \cdot N(R)$$

$$(19b) \quad = K'' \left\{ b \frac{P_t G_t G_r \lambda^2}{k T_e B} \frac{F_t^2 \cdot F_r^2}{64 \pi^3 R^4} \frac{\tau c}{2} \Phi A \right\}^{m-1} \cdot R \cdot N.$$

(b) The exponential law:

$$(20) \quad p(\sigma)d\sigma = \frac{1}{\sigma_m} e^{-\sigma/\sigma_m} d\sigma$$

where σ_m = mean cross section. Hence

$$(21) \quad \int_{\sigma_L}^{\infty} p(\sigma)d\sigma = e^{-\sigma_L/\sigma_m} \equiv f\{\sigma_L\}$$

and

$$(22a) \quad D' = e^{-\sigma_L/\sigma_m} \cdot R \cdot N(R)$$

$$(22b) \quad = \left\{ \exp \left[- \frac{1}{b \sigma_m} \frac{k T_e B}{P_t G_t G_r \lambda^2} \frac{64 \pi^3 R^4}{F_t^2 F_r^2} \frac{2}{\tau c} \frac{1}{\Phi A} \right] \right\} \cdot R \cdot N.$$

The slope of the best-fitting straight line in Fig. 2A yields the value of $m-1$. From several selected periods, the quantity $m-1$ is found to lie in the region 0.5 to 0.9, and a representative value of 0.67 will be adopted. This result, $m = 1.67$, is consistent with earlier work by the author (McNamara 1954) at Saskatoon where the value $m = 1.5$ was obtained using a much different method of analysis on data obtained from a high-power short-pulse radar at 56 Mc/s. In the present instance, additional checks were also made by shorter periods of operation with simultaneous recordings of 50-km gate length

covering the interval 700–750 km and the standard 800-km gate length covering 300–1100 km. The distributions obtained over the period 1 December 1958 to 30 January 1959 with short and long gates are shown in Fig. 3. The close correspondence of the slopes of the two curves supports the validity of the application of the long-gate statistics to the general analysis. A further check on the exponent was made using a logarithmic receiver recording a 30-db range of signal, yielding the value of $m = 1.5$.

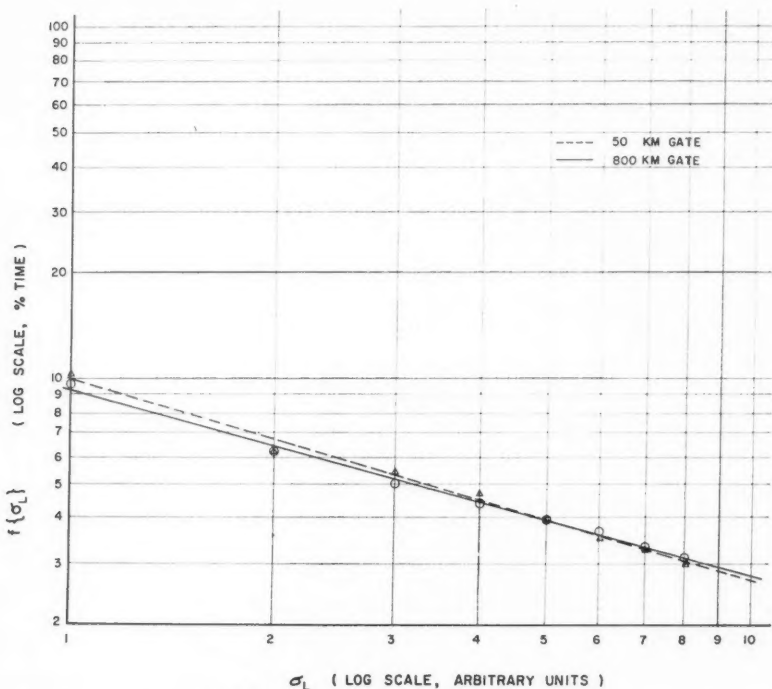


FIG. 3. Comparison of cross-section distributions obtained from simultaneous operation of narrow and wide gates centered at a range of 700 km. The slopes $m-1$ of the lines are 0.58 and 0.53 respectively.

Equation 19 or 22 may thus be taken as giving the variation of echo occurrence with range, and giving a measure of the functional dependence of occurrence rate on the geometry, equipment parameters, and antenna patterns. Plots of equations 19 and 22 for two different combinations of antenna heights are shown in Fig. 5, corresponding to case (ii). Modification of equations 19 and 22, by deleting the multiplicative R factor and changing the R^{-4} to R^{-3} , results in equations appropriate to case (i). These are plotted in Fig. 4. For all sample calculations the values $N(R) = 1$, $R_0 = 300$ km, $R_1 = 500$ km were used. In each figure, the A curves correspond to the

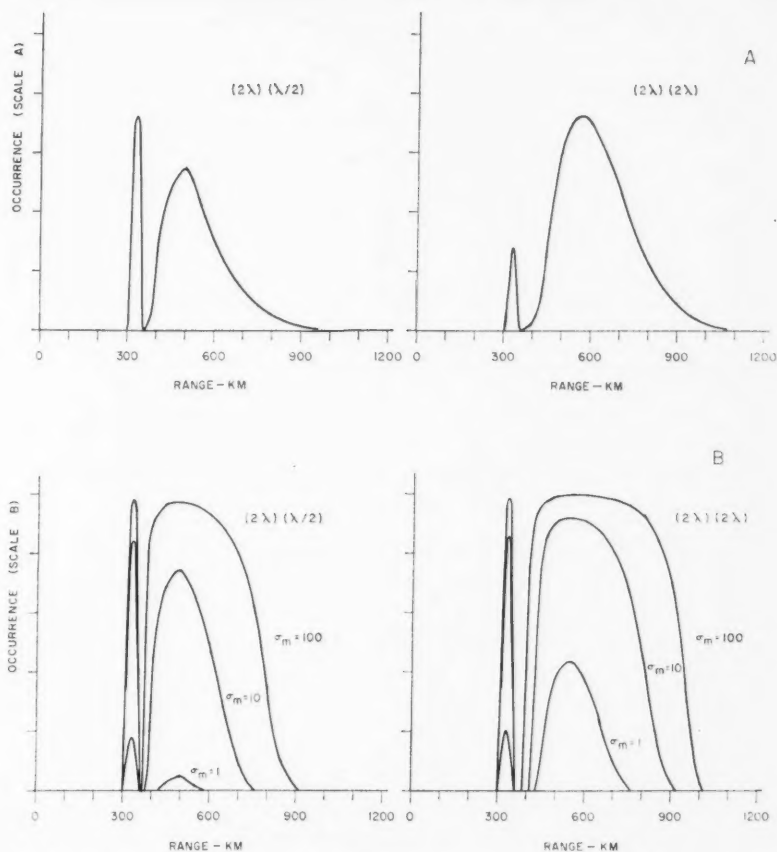


FIG. 4. Theoretical echo range distributions for two radar systems differing only in the heights of their transmitting-receiving antenna configurations above the ground. Calculations are based on the assumptions of completely distributed targets, and for a power law (A) and an exponential law (B) of target cross sections.

inverse power law distribution of target cross sections, and the *B* curves correspond to the exponential law.

For the inverse power law, the shape of the echo distribution is independent of the radar sensitivity factors, the vertical scale varying as the 0.67 power of the sensitivity. For the exponential law, the shape as well as the vertical scale varies with the sensitivity, and also with the mean of the target cross section distribution.

As indicated in Tables I and II both forms yield distributions and occurrences not unlike the observational data, provided an appropriate choice is made for σ_m in the exponential law. Additional data from a $(2\lambda) (\lambda/2)$ system

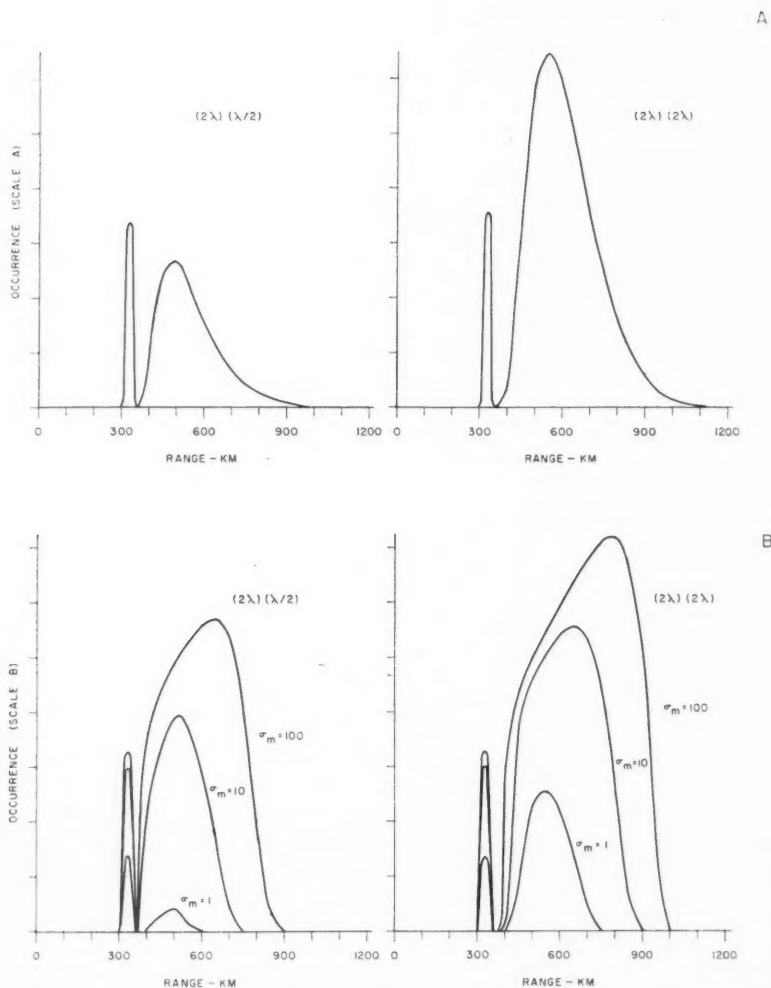


FIG. 5. Theoretical echo range distributions for two radar systems differing only in the heights of their transmitting-receiving antenna configurations above the ground. Calculations are based on the assumptions of localized targets, and for a power law (A) and an exponential law (B) of target cross sections.

TABLE I

Echo occurrences derived from Fig. 4 for the case of completely distributed targets (case (i))*

Relative mean target cross section	Area under curve*		Peak value of first lobe*			
	(2λ) (λ/2) configuration	Ratio →	(2λ) (2λ) configuration	(2λ) (λ/2) configuration	Ratio →	(2λ) (2λ) configuration
A. Power law for cross section						
	100	2.9	290	100	2.6	260
B. Exponential law for cross section						
$\sigma_m = 1$	3.7	14	52	6.7	10	67
$\sigma_m = 10$	100	2.2	220	100	1.5	150
$\sigma_m = 100$	240	1.5	360	150	1.3	200

*Normalized to the value 100 for the reference configuration (A) (2λ) (λ/2), (B) (2λ) (λ/2) with $\sigma_m = 10$.

TABLE II

Echo occurrences derived from Fig. 5 for the case of localized targets (case (ii))*

Relative mean target cross section	Area under curve*			Peak value of first lobe*		
	(2λ) (λ/2) configuration	Ratio →	(2λ) (2λ) configuration	(2λ) (λ/2) configuration	Ratio →	(2λ) (2λ) configuration
A. Power law for cross section						
	100	2.4	240	100	2.4	240
B. Exponential law for cross section						
σ _m = 1	9.1	5.7	52	11	6	66
σ _m = 10	100	1.8	180	100	1.4	140
σ _m = 100	210	1.6	330	150	1.2	180

*Normalized to the value 100 for the reference configuration (A) (2λ) (λ/2), (B) (2λ) (λ/2) with $\sigma_m = 10$.

with a 20-db variability in sensitivity suggests that the exponential law can be fitted more accurately over a larger dynamic range. Mathematically, the exponential law may be more convenient since all its moments are finite and it can be normalized. On the other hand, the inverse power formulation may often be convenient for comparison of system parameters since no assumptions nor measurements need be made concerning the magnitude of the cross-section scale.

It should be noted that although the equations contain a radio wavelength term (λ^2), they do not give the frequency dependence of the echo occurrence. The λ^2 term arises from the conversion of effective area of receiving antenna into antenna gain; the true wavelength dependence of the echoes is hidden in the cross-section term, σ , and is not considered in this paper.

6. INTEGRATED ECHO OCCURRENCE

The formulas of the preceding section were developed in terms of the detailed echo occurrence defined by the range and time division discussed in Section 3. Also of interest, is the description of occurrence in terms of time alone, any echo or echoes present at a given time satisfying the definition of an occurrence. The formulas may be used as a guide in deriving these indices but cannot be confidently applied because of the unknown correlation of echo occurrence in space and time. In fact, the geographical correlation distance of

target occurrence is often large and the probability of echo occurrence in adjacent range increments is not independent. If the echoes in each range increment were statistically independent in time, the range-integrated echo probability would be proportional to the area under the D' curve.

This may be seen from the following argument. Assume that echoes in adjacent range increments occur independently in time and let the probability that range increment i will have an echo be D'_i , and the probability that all increments will simultaneously fail to have an echo is $\prod_{i=1}^n (1-D'_i)$. Our definition of an echo occurrence on a purely time basis is that at least one increment does contain an echo. This probability is $1 - \prod_{i=1}^n (1-D'_i)$, which, for small probabilities, $D_i \ll 1$, may be expanded

$$1 - \prod_{i=1}^n (1-D'_i) = 1 - (1 - \sum D'_i + \text{higher-order terms}) \approx \sum D'_i.$$

This is simply the area under the distribution curve of equations 19 and 22, for which examples are plotted in Figs. 4 and 5. The areas under these curves are tabulated in Tables I and II and may be taken as an approximation to the relative amount of echo which will be observed.

7. NUMERICAL EXAMPLES

In Tables I and II, corresponding to cases (i) and (ii) of distributed and localized targets, are given the areas under the curves and the heights of the peak of the main lobe. The tabulated values have been normalized to 100 for the reference configuration (2λ) ($\lambda/2$) with $\sigma_m = 10$. It should be noted that the computations were made on the basis of a uniform occurrence of targets all over the ionosphere, $N(R, \phi) = 1$.

Experimentally, for two such radar systems operating simultaneously at Ottawa over a period of 2 years, the occurrence ratio was found to be 2.5 to 1. Although no allowance has been made for small system gain differences, nor for the naturally increasing occurrence of aurora with range toward the auroral zone, the agreement with the tabular values is satisfactory.

CONCLUSION

Expressions have been derived relating the radar parameters to the auroral echo statistics observed. For this to be done, it was necessary to adopt practical definitions of 'echo occurrences' and to interpret the appropriate activity indices. The sensitivity of the indices is demonstrated by equations 19 and 22 and Figs. 4 and 5, and indicates the necessity for caution in the comparison of indices from different systems and the need for accuracy in determination and stabilization of the radar parameters.

REFERENCES

- CURRIE, B. W., FORSYTH, P. A., and VAWTER, F. E. 1953. *J. Geophys. Research*, **58**, 179.
 KERR, D. E. 1951. Propagation of short radio waves, M.I.T. Radiation Laboratory Series, Vol. 13.
 McNAMARA, A. G. 1954. Ph.D. Thesis, University of Saskatchewan, Saskatoon, Saskatchewan.
 ——— 1958. *Can. J. Phys.* **36**, 1.
 McNAMARA, A. G. and CURRIE, B. W. 1954. *J. Geophys. Research*, **59**, 279.
 UNWIN, R. S. and GADSDEN, M. 1957. *Nature*, **180**, 1469.

LIQUID-SOLID INTERFACE SHAPE OBSERVED IN SILICON CRYSTALS GROWN BY THE CZOCHRALSKI METHOD¹

W. D. EDWARDS

ABSTRACT

A study has been made of the macroscopic structure of the liquid-solid interface which exists during growth of silicon crystals by the Czochralski method. In two crystals the interface was seen to contain a (111) facet. The development of such facets is discussed with reference to current crystal growth theories.

INTRODUCTION

The shape and structure of the liquid-solid interface during growth of silicon single crystals is of great importance and has been discussed by a number of authors (Cressell and Powell 1957; Rosi 1958; and Tiller 1958). For example, Cressell (1957) and Rosi (1958) have observed that an interface which is planar or slightly convex towards the liquid leads to crystals with a minimum dislocation density. In this laboratory interfaces have been observed which are parallel, over macroscopic distances, to the (111) planes lying normal to the growth direction.

The interface shape may be observed in a number of ways. It may be viewed directly by rapidly separating the growing crystal from the melt during growth (Elbaum and Chalmers 1955). The possibility that liquid adhering to the crystal will solidify after decantation and the fact that the interface shape is observed at one position only are the limitations of this method. A second method of revealing interface shape requires the addition of volatile impurities to a melt under vacuum from which a crystal is being grown by the Czochralski technique. For example, a silicon crystal grown from a melt containing boron as an impurity will be *P*-type, but when an excess of antimony is added to the melt the growing crystal becomes *N*-type. Under vacuum, antimony evaporates rapidly compared with boron and the growing silicon crystal reverts to *P*-type (Bradshaw and Mlavsky 1956). The grown crystal may be sectioned longitudinally, i.e. parallel to the growth axis, ground and etched to reveal the *P-N* and *N-P* junctions. The interface shape at the time of the addition of the antimony is shown by the shape of the *P-N* junction. In this way the interface shape at a number of times during the growth of the crystal may be studied. Rate-grown junctions (Tanenbaum *et al.* 1955) may also be used to give a continuous record of the interface shape during crystal growth. However, this method imposes stringent conditions on the growth rate of the crystal and on the impurities added to the melt.

The most useful and convenient method of interface examination makes use of the variations in crystal composition which occur during growth. Unless special precautions are taken during growth, Czochralski-type silicon crystals

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exhibit variations in resistivity and oxygen content both radially and longitudinally. The longitudinal variations are closely related to the rotation rate and in many instances their period equals the growth per revolution of the crystal. If a crystal is cut longitudinally and if the exposed face is ground and etched these variations or striations are revealed as corrugations on the surface. The striations give a revolution-by-revolution macroscopic picture of the interface shape during crystal growth. Striations with a separation of 0.001 cm have been resolved. In a variation of this method Camp (1954) has used a copper-plating technique to delineate resistivity striations in germanium and has successfully resolved striations with a separation of just less than 1 mm.

EXPERIMENTAL

Six crystals were examined; these were grown by the Czochralski method with the solid-liquid interface convex towards the liquid. Each crystal was cut longitudinally and then the newly exposed faces were ground and etched as described in the Appendix. The corrugations produced on the flat surface by the etch had a separation equal to the growth per revolution of the crystal and a curvature as expected for an interface which was convex towards the liquid.

Two crystals examined had two distinct breaks in each of the striations and the sections of the striations between the breaks were straight lines (Figs. 1a and 1b). Typical straight line sections were 0.45 cm long on striations with a radius of curvature of 2.5 cm. Near to the top of the crystal, as shown in Fig. 1a, the reduced radius of curvature of the interface restricted the development of these 'flats' on the interface and caused an increase in the change of direction at the breaks in the striations to an observed maximum of $7\frac{1}{2}^\circ$. These straight line sections of the striations were observed to be perpendicular to the [111] direction which was near to the growth axis of the crystal. Each of the two crystals was cut again to bisect the straight line striations and to reveal a second face normal to the original section. These second faces were also ground and etched in order to reveal the striations. The two flat faces of each crystal were masked with 'Halo' wax and the remaining crystal surface was etched in hot caustic soda which is a structure-sensitive etch for silicon. An optical goniometer was used to show that the (111) planes approximately normal to the axis of growth would give traces in the two sectioned faces parallel to the straight line sections of the striations.

The growth axis of one crystal was 4.5° from the [111] direction and this angle is shown as θ in Fig. 1a. The growth and rotation rates of this crystal were 8.4×10^{-4} cm/sec and 4.6 r.p.m., respectively, which gave a striation separation of 1.1×10^{-2} cm. The crystal was *P*-type with a resistivity of approximately 0.4 ohm-cm. The exact growth conditions of the second crystal* are not known. This second crystal was *N*-type with a resistivity of approxi-

*Kindly donated by D.R.B. to Northern Electric Co. Ltd.

FIG. 1a. The form of the striations seen after etching a section of a silicon crystal which had been cut parallel to the [111] growth axis. The lines *x* and *y* indicate the extent of the (111) flats.

FIG. 1b. Photograph of the striations taken at the approximate position of the inset marked near the top left corner of Fig. 1a.



Fig. 1b.

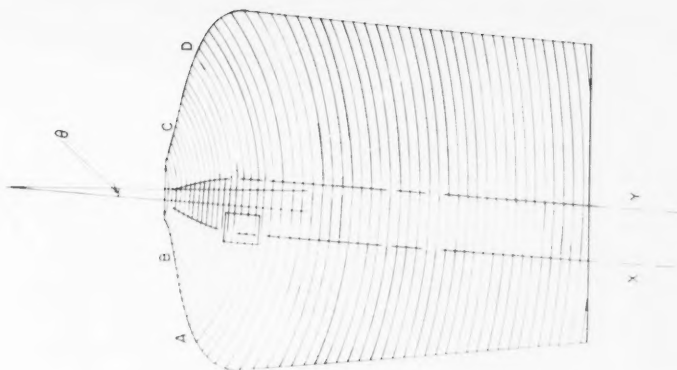


Fig. 1a.



mately 20 ohm-cm and the growth axis was 4° from the $[111]$ direction. The striation separation varied between 0.001 cm and 0.01 cm.

On this second crystal it was observed that where the diameter was increasing rapidly, i.e. in the sections AB and CD (Fig. 1a), the striations abruptly changed direction within approximately 0.1 mm from the edge of the section (Fig. 2). These were probably traces of other $\{111\}$ planes but unfortunately poor masking of the sample led to their loss during etching and before measurements were made.

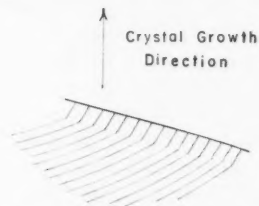


FIG. 2. An enlarged drawing of the crystal-section edge in the region CD of Fig. 1a. The abrupt change in striation direction near to the surface is indicated.

DISCUSSION

With crystals grown by the Czochralski method the $\{111\}$ planes often give rise to facets on the crystal (Billig 1955). Crystals pulled in the $\langle 111 \rangle$ direction have three such facets spaced symmetrically around the circumference of the crystal; the fourth $\{111\}$ plane which is normal to the growth direction lies approximately parallel to the liquid-solid interface. The $\{111\}$ planes are the most closely packed in the silicon structure. Growth in a direction normal to these planes is slow because of the low accommodation coefficient (Chalmers 1954) whereas growth by lateral extension of the $\{111\}$ planes is preferred (Tiller 1958; Billig 1955). The preferred directions of lateral growth in the (111) plane are the $[2\bar{1}\bar{1}]$, $[\bar{1}2\bar{1}]$, and $[\bar{1}\bar{1}2]$ directions (Billig 1955) which give rise to the three symmetrically placed spikes commonly observed when a crystal is pulled in the $[111]$ direction.

It is the (111) set of planes lying perpendicular to the growth axis of a $[111]$ crystal which has been detected on a macroscopic scale by the etching experiments and which normally does not give rise to any visual characteristics of a crystal. In two crystals the interface was found to be limited over macroscopic distances by the densely packed (111) planes which are approximately normal to the growth axis.

The temperature gradient existing at the interface during crystal growth can be estimated only approximately. Calculations made by Billig (1955, 1956) are inapplicable because the considerable radiation received by the ingot from the adjacent melt and susceptor is ignored; this leads to values of temperature gradient which are much too high. With growth from a crucible the temperature gradient decreases as crystal growth proceeds. Observations made with a pyrometer, at pertinent times during crystal growth, indicated a temperature drop of 150°C in the first centimeter from the liquid-solid interface. If it is assumed that

- (a) the gradient actually existing at the interface is $150^{\circ}/\text{cm}$,
- (b) the curved portions of the liquid-solid interface are coincident with the freezing point isotherm, and
- (c) the liquid-solid interface has an approximately constant radius of curvature,

then in the two crystals considered there is approximately 1.5°C of supercooling at the center of the (111) flats.

Nucleation of (111) planes will occur at this point. With an interface slightly convex towards the liquid these (111) planes will grow outwards in a stepwise manner (Tiller 1958; Elbaum and Chalmers 1955) to the limiting diameter of the crystal. If the interface is appreciably curved, as in Fig. 1a, the completion of a (111) layer will take several revolutions of the growing crystal. However, if the interface is concave towards the liquid there is the possibility of nucleation at several points around the interface periphery. With nucleation at the periphery the (111) planes grow inwards in a stepwise manner to completion. At the interface periphery there is a liquid-gas and a liquid-solid interface. Twinning and heterogeneous nucleation are likely to occur here, possibly because the lattice spacing is not quite normal in the last few atomic layers near to the solid-gas interface and also because of the presence of minute particles of oxide or other impurity, for example, silicon carbide if a carbon susceptor and heater are used. The growth of strays and twins into the main body of the crystal is thus encouraged by the concave interface and this has been discussed by Chalmers (1953) and Bolling *et al.* (1956).

In conclusion, lattice misfits and twinning are more likely to occur if (111) planes nucleate at the crystal periphery and grow inwards rather than if nucleation occurs near the crystal center with growth outwards to completion as is the case with an interface which is slightly convex to the melt. Results have been given which suggest that the (111) planes normal to the crystal growth axis do play an important role in the growth mechanism. In equilibrium the interface will be composed of {111} planes as they have the lowest accommodation coefficient and equilibrium temperature. Consequently, an interface limited by the (111) plane normal to the growth axis is most likely to occur in crystals which are pulled slowly from a melt in which the temperature gradients are small. This picture of crystal growth, which especially applies to the two instances cited, is in agreement with the observations of Cressell and Powell (1957), Rosi (1958), Bolling *et al.* (1956), and Billig (1956) that the least twinning, lineage, and the lowest density of dislocations occur when the interface is planar or slightly convex towards the liquid during crystal growth.

APPENDIX

The etching of silicon by a mixed nitric acid-hydrofluoric acid etch is basically a two-step process. The HNO_3 oxidizes the silicon and the HF dissolves the oxide re-exposing the silicon surface to the action of the HNO_3 (Robbins and Schwartz 1959). The oxidation is the structure-sensitive step and suitable control of the HNO_3 content leads to maximum information regarding the structure and composition of the silicon.

For the delineation of striations the sample surfaces to be studied were first ground and then chemically polished in a mixture of 3 parts HNO_3 (70%) and 1 part HF (48%). The sample was then placed in 40 cc of HF (48%) and approximately 0.03 cc (one drop) of HNO_3 (70%) was added to the solution every 30 seconds for a total time of from 5 to 15 minutes. Illumination of the specimen during the etching process greatly enhanced the delineation of the striations. The rate of addition of drops and time of etch were not critical and the most suitable conditions for silicon of a given resistivity were experimentally determined. A slow oxidation step appeared to be essential and if the sample was immersed in a comparable HNO_3 - HF mixture a fast reaction took place with evolution of considerable heat and very poor, if any, delineation of striations.

REFERENCES

- BILLIG, E. 1955. *Proc. Roy. Soc.* **229**, 346.
——— 1956. *Proc. Roy. Soc.* **235**, 37.
BOLLING, G. F., TILLER, W. A., and RUTTER, J. W. 1956. *Can. J. Phys.* **34**, 234.
BRADSHAW, S. E. and MLAVSKY, A. I. 1956. *J. Electronics*, **2**, 134.
CAMP, P. R. 1954. *J. Appl. Phys.* **25**, 459.
CHALMERS, B. 1953. *Can. J. Phys.* **31**, 132.
——— 1954. *Trans. AIME*, **200**, 519.
CRESSSELL, L. G. and POWELL, J. A. 1957. *Progress in Semiconductors*, **2**, 139.
ELBAUM, C. and CHALMERS, B. 1955. *Can. J. Phys.* **33**, 196.
ROBBINS, H. and SCHWARTZ, B. 1959. *J. Electrochem. Soc.* **106**, 505.
ROSI, F. D. 1958. *R. C. A. Rev.* **19**, 349.
TANENBAUM, M., VALDES, L. B., BUEHLER, E., and HANNAY, N. B. 1955. *J. Appl. Phys.* **26**, 686.
TILLER, W. A. 1958. *J. Appl. Phys.* **29**, 611.

AN EMISSION SYSTEM OF THE IO MOLECULE¹

R. A. DURIE,² F. LEGAY,³ AND D. A. RAMSAY

ABSTRACT

The "methyl iodide flame bands", lying in the region 4100 to 6300 Å, have been photographed using a 21-ft concave grating spectrograph. The bands are shown to arise from an $A^2\Pi \rightarrow X^2\Pi$ transition of the IO molecule. Rotational and vibrational analysis of the bands has been carried out and the molecular constants of IO obtained.

INTRODUCTION

A number of red-degraded bands, now known as the "methyl iodide flame bands", was first observed by Vaidya (1937) in emission from a flame of methyl iodide mixed with methyl alcohol or coal gas. The bands were analyzed into two systems, A and B, and were tentatively assigned to the IO or CI molecule. Coleman, Gaydon, and Vaidya (1948) obtained the bands in emission from an oxyhydrogen flame to which iodine was added, thus supporting the assignment to IO. These authors observed approximately 40 bands in the region 4100 to 6300 Å and showed that all the bands could be arranged into one system instead of two. Vibrational constants were given but no rotational analysis was attempted since the bands were observed only with low resolution.

Durie and Ramsay (1958) observed six bands of the same system in absorption during the flash photolysis of mixtures of iodine vapor and oxygen. The bands were observed with high resolution but no rotational analysis of the absorption bands was attempted since the same bands, extending to much higher J values, were also observed in emission from an oxyhydrogen flame to which methyl iodide was added. Most of the bands reported by Coleman, Gaydon, and Vaidya were rephotographed under high resolution by Durie and Ramsay. The rotational and vibrational analysis of these bands forms the main subject of the present paper and confirms the assignment of the bands to the IO molecule.

EXPERIMENTAL

The source used to excite the methyl iodide flame bands consisted of a diffusion flame of hydrogen, saturated with methyl iodide vapor at room temperature, burning in an atmosphere of oxygen. The bands were photographed using the second order of a 21-ft concave grating spectrograph and Eastman Kodak 103a0, 103aD, 103aB, and 103aF plates. The exposure times varied from 1 to 5 hours. An iron arc was used to provide a reference spectrum.

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PLATE I

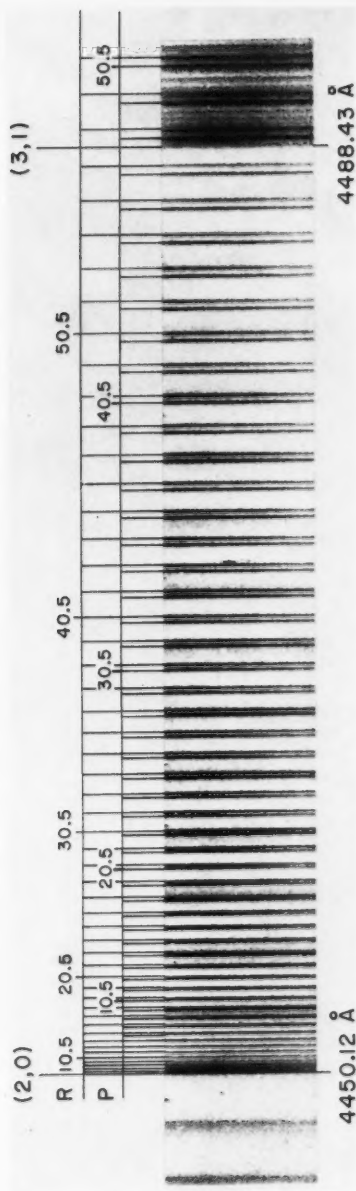


FIG. 1. Enlargement of the $(2,0)$ band of IO showing the assignments of the rotational lines.

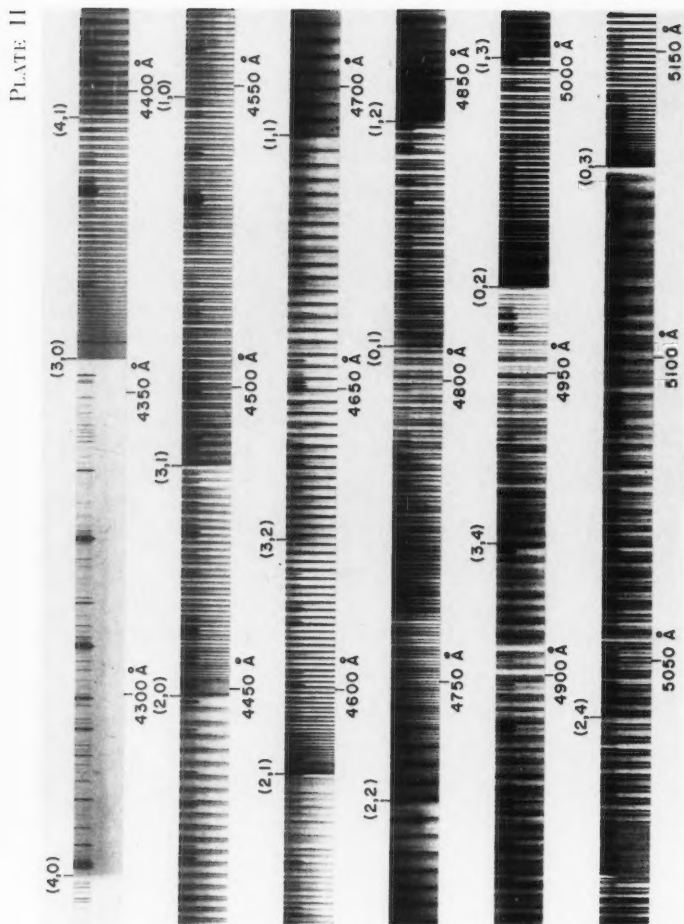


FIG. 2

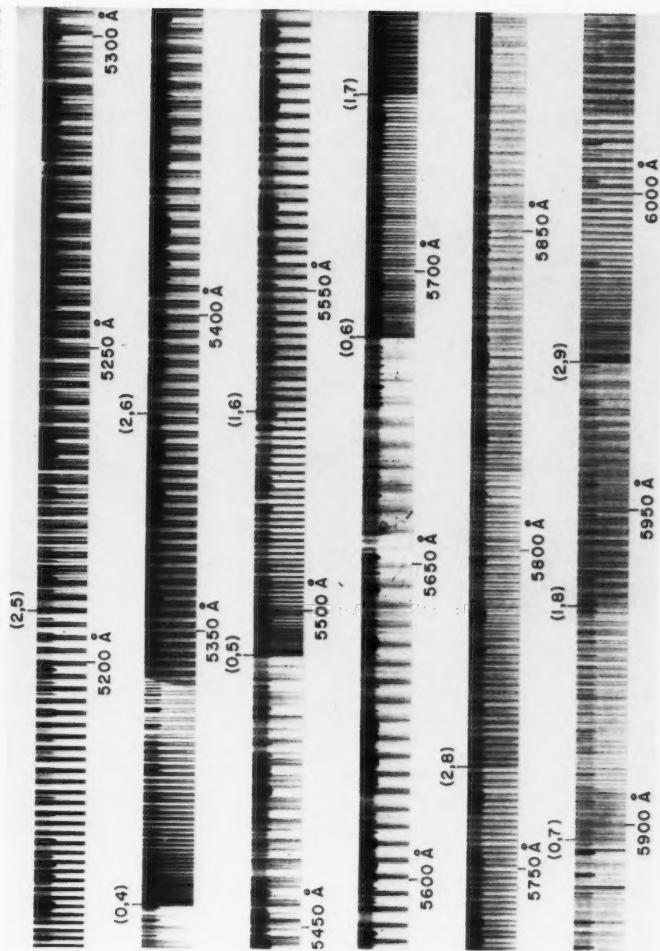


FIG. 2. Spectrum of IO observed in emission from an oxyhydrogen flame to which methyl iodide was added. The bands were photographed using the second order of a 21-ft concave grating spectrograph. (The discontinuities near 5020, 5340, and 5650 Å are due to plate joins.)



A reproduction of the spectrum is given in Fig. 2; an enlargement showing the rotational structure of one of the bands and the rotational assignments is given in Fig. 1. It may be seen from Fig. 2 that many of the bands have discrete and well-resolved rotational structures while others are completely diffuse or show a distinct broadening of the rotational lines. The presence of diffuseness in certain bands is due to predissociation in the excited state. Using the vibrational assignments of Coleman, Gaydon, and Vaidya we find that bands with $v' = 1, 4$, and 5 are completely diffuse, bands with $v' = 3$ have rotational lines which are slightly broader than the slit width, while bands with $v' = 0$ and 2 have rotational lines which are sharp. These different types of rotational structure may be seen (Fig. 2) by comparing the rotational structures of the $(4,0)$, $(3,0)$, and $(2,0)$ bands.

Wavelength measurements were carried out using a comparator equipped with a photoelectric scanning device of the type described by Tomkins and Fred (1951). Standard wavelengths were taken from the M.I.T. wavelength tables (Harrison 1939) and were combined with the vacuum corrections of Edlén (1953). The rotational lines of eight bands were measured and the vacuum wavenumbers and assignments are given in Table I. The wavelengths of the sharp band heads are given in Table II; the band head measurements of Coleman, Gaydon, and Vaidya are also given. Both sets of measurements are compared with the wavelengths of the band heads calculated from our final molecular constants.

ANALYSIS

The electronic transition responsible for the IO bands is expected to be of the type ${}^2\Pi_1(a)-{}^2\Pi_1(a)$ by analogy with the known transitions for ClO and BrO (Durie and Ramsay 1958). For Hund's case (a) coupling, each band splits into two well-defined subbands, viz. ${}^2\Pi_{3/2}-{}^2\Pi_{3/2}$ and ${}^2\Pi_{1/2}-{}^2\Pi_{1/2}$, and each subband consists predominantly of a single P and R branch and a very weak Q branch. For IO, the discrete bands show single P and R branches but no Q branches were detected. Moreover, for each band, only one of the subbands was observed, presumably due to a large spin splitting in the upper state. This is not surprising in view of the large doublet splitting in the ground state of the iodine atom, viz. 7598 cm^{-1} . It has been assumed that the observed subbands are of the type ${}^2\Pi_{3/2}-{}^2\Pi_{3/2}$ although it should be pointed out that it was not possible to verify this assumption by observation of the P and R branches to the lowest J values.

The various molecular constants were determined by the following standard procedures (Herzberg 1950).

1. Determination of B_v and D_v

The rotational constants B_v and D_v were obtained from the combination differences $\Delta_2 F'(J) = R(J) - P(J)$ and $\Delta_2 F''(J) = R(J-1) - P(J+1)$ by plotting $\Delta_2 F/(J+\frac{1}{2})$ against $(J+\frac{1}{2})^2$. The values of B and D for $v' = 0$ and 2 and $v'' = 0$ and 2 were obtained using data from more than one band. These values are considered to be more accurate than those obtained for the other vibrational levels and are given in Table III. The other B and D values were refined in the manner described in Sections 2 and 3.

TABLE I
Vacuum wavenumbers and rotational assignments for the $^2\Pi_{3/2}-^2\Pi_{3/2}$ subbands of IO

J	(0,2)		(2,2)		(2,0)		(3,0)	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
2.5				21130.25				
3.5				129.10				
4.5				127.88				
5.5				126.49	22470.76			
6.5		20130.74	21134.09	125.00	470.24			
7.5		129.27	133.65	123.38	469.64	22459.86		
8.5	20137.65	127.74	133.09	121.61	458.02		22951.26	
9.5	137.03	126.10	132.46	119.77	467.95	456.05	948.86	22937.25
10.5	136.46	124.22	131.63	117.77	466.89	453.93	947.77	935.10
11.5	135.56	122.40	130.72	115.63	465.71	451.66	946.46	932.69
12.5	134.67	120.34	129.67	113.38	464.39	449.26	944.99	930.27
13.5	133.59	118.26	128.48	110.99	462.92	446.71	943.49	927.52
14.5	132.45	115.98	127.18	108.46	461.32	444.04	941.83	924.85
15.5	131.14	113.62	125.74	105.85	459.57	441.22	939.96	921.86
16.5	129.83	111.15	124.16	103.07	457.70	438.27	—	918.80
17.5	128.32	108.57	122.49	100.18	455.67	435.18	935.84	915.64
18.5	126.74	105.88	120.69	118.72	453.52	431.95	933.55	912.27
19.5	124.98	103.02	118.72	116.66	451.21	428.58	931.15	908.81
20.5	123.15	100.07	116.66	114.46	448.80	425.07	928.57	905.17
21.5	121.17	97.00	114.46	112.15	446.24	421.43	925.83	901.40
22.5	119.08	93.83	112.15	109.68	443.51	417.65	922.98	897.46
23.5	116.91	90.53	109.68	108.16	440.66	413.73	919.99	893.36
24.5	114.57	87.15	107.11	104.40	437.66	409.66	916.87	889.21
25.5	112.13	83.61	104.40	101.55	434.55	405.46	913.58	884.87
26.5	109.60	79.99	101.55	98.51	431.29	401.14	910.11	880.34
27.5	106.90	76.22	98.51	95.56	427.84	396.66	906.57	875.70
28.5	104.11	72.34	95.56	92.42	424.36	392.05	902.85	870.93
29.5	101.23	68.32	92.42	89.35	420.67	387.30	898.97	866.00
30.5	98.23	64.19	89.35	86.18	416.86	382.41	894.94	860.92
31.5	95.09	59.98	86.18	83.01	412.91	377.38	890.78	855.71
32.5	91.78	55.66	83.01	79.75	408.81	372.22	886.49	850.32
33.5	88.42	51.17	79.75	76.30	404.58	366.93	882.03	844.85
34.5	84.97	46.59	76.30	72.81	400.21	361.49	877.44	839.18
35.5	81.32	41.88	72.81	69.19	395.71	355.90	872.71	833.38
36.5	77.62	37.05	69.19	65.41	391.06	350.20	867.81	827.45
37.5	73.79	32.15	65.41	61.67	386.27	344.35	862.77	821.35
38.5	69.83	27.12	61.67	57.90	381.34	338.50	857.60	815.13
39.5	65.73	22.05	57.90	54.02	376.29	332.24	852.27	808.76
40.5	61.56	16.69	54.02	50.08	371.08	325.98	846.81	802.25
41.5	57.27	11.28	50.08	46.09	365.74	319.56	841.20	795.57
42.5	52.83	6.05	46.09	42.06	360.26	313.03	835.43	788.76
43.5	48.29	0.00	42.06	38.01	354.65	306.35	829.50	781.77
44.5	43.64	19994.38	38.01	34.00	348.90	299.53	823.45	774.69
45.5	38.86	988.56	34.00	30.00	343.01	292.57	817.26	767.45
46.5	33.98	982.58	30.00	26.00	336.97	285.48	810.91	760.04
47.5	28.97	976.49	26.00	22.00	330.80	278.25	804.42	752.52
48.5	23.84	970.24	22.00	18.00	324.51	270.92*	797.79	744.82
49.5	18.57	963.97	18.00	14.00	318.05	263.41*	791.00	737.00
50.5	13.26	957.50	14.00	10.00	311.47		784.05	729.02
51.5	7.77	950.99	10.00	6.00	304.73		776.97	720.90
52.5	2.24	944.30	6.00	2.00	297.90		769.74	712.63
53.5	19996.47	937.56	2.00	0.00	291.01		762.38	704.23
54.5	990.62	930.62	0.00	0.00	284.12		754.85	695.67
55.5	984.70	923.59	963.89	903.91	277.49*		747.17	686.95
56.5	978.63	916.45	957.21	896.24	269.05*		739.37	678.12
57.5	972.46	909.16	950.44	888.40	261.65*		731.40	669.12
58.5	966.18	901.86	943.52	880.44			723.26	659.97
59.5	959.74	894.42	936.48	872.34			715.01	650.66
60.5	953.22	886.60	929.32	864.12			706.59	641.23
61.5	946.58	879.01	922.00	855.78			698.04	631.63
62.5	939.81	871.21	914.56	847.29			689.34	621.90
63.5	932.95	863.26	907.04	838.72			680.47	612.03
64.5	925.95	855.24	899.36	830.05			671.45	601.99
65.5	918.85	847.02	891.55	821.23			662.30	591.83
66.5	911.70	838.68	883.49	812.16			653.00	581.50
67.5	904.21	830.37*	875.50	802.66*			643.56	570.99
68.5	896.81	822.00*	867.40	793.63*			633.90	560.41
69.5	889.25		859.03	784.16*			624.17	549.67
70.5	881.56		850.57				614.27	538.77
71.5	873.83		841.94				604.22	527.64
72.5	865.92		833.29				594.00	516.50
73.5	857.66		824.41				583.63	505.08
74.5	849.55		815.45				573.10	493.56
75.5	841.56		806.22				562.47	481.97
76.5	832.75		797.14*				551.67	470.34
77.5	824.57*		786.37*				540.72	458.75
78.5	815.43*						529.48	446.16
79.5							518.28	
80.5								

*Denotes overlapped line.

TABLE I (Concluded)

Vacuum wavenumbers and rotational assignments for the $^2\Pi_{3/2}-^2\Pi_{3/2}$ subbands of IO

J	(2,9)		(0,6)		(0,4)		(0,3)	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
2.5								
3.5								
4.5								
5.5								
6.5								
7.5								
8.5	16736.02	726.36			18830.38			
9.5	735.76	724.97			829.09			
10.5	735.37	723.52			827.77			
11.5	734.91	721.97	17570.51	17559.21	836.39		19482.54	19472.37*
12.5	734.31	720.31	569.18	567.67	835.74		481.92	470.75*
13.5	733.70	718.60	569.18	566.06	835.14		481.32	469.02*
14.5	732.95	716.74	568.55	564.31	834.54		480.56	467.18*
15.5	732.07	714.86	567.82	562.39	833.95		479.73	465.24*
16.5	731.23	712.88	566.94	560.52	832.87		478.78	463.20*
17.5	730.18	710.80	566.17	558.45	831.85		477.72	461.01*
18.5	729.11	708.62	565.09	546.38	830.78		476.53	458.72*
19.5	727.92	706.39	564.00	544.16	829.59		475.27	456.33*
20.5	726.68	704.05	562.73	541.86	828.25		473.89	453.83*
21.5	725.32	701.62	561.45	539.42	826.83		472.37*	451.21*
22.5	723.87	699.10	559.67	536.94	825.34		470.75*	448.63
23.5	722.34	696.47	558.56	534.38	823.69		469.02*	445.83
24.5	720.73	693.82	556.97	531.73	821.97		467.18*	442.86
25.5	719.04	691.06	555.28	528.96	820.16		465.24*	439.80
26.5	717.24	688.18	553.56	526.05	818.20		463.20*	436.63
27.5	715.35	685.23	551.67	523.06	816.14		461.01*	433.35
28.5	713.38	682.16	549.71	520.06	814.02		458.72*	429.97
29.5	711.35	679.05	547.67	516.90	811.77		456.33*	426.50
30.5	709.21	675.83	545.47	513.66	809.39		453.83*	422.87
31.5	707.01	672.54	543.23	510.31	806.94		451.21*	419.15
32.5	704.63	669.16	540.98	506.88	804.33		448.33	415.32
33.5	702.23	665.61	538.49	503.35	801.64		445.50	411.38
34.5	699.79	662.10	535.93	499.71	798.84		442.52	407.33
35.5	697.14	658.47	533.31	496.00	795.96		439.44	403.16
36.5	694.44	654.71	530.56	492.20	792.97		436.28	398.89
37.5	691.76	650.91	527.75	488.30	789.86		432.99	394.50
38.5	688.89	646.95	524.86	484.28	786.63		429.56	389.99
39.5	685.96	643.01	521.84	480.16	783.32		426.03	385.41
40.5	682.92	638.89	518.74	476.03	779.86		422.42	380.67
41.5	679.81	634.71	515.55	471.77	776.36		418.66	375.86
42.5	676.67	630.42	512.29	467.37	772.74		414.81	370.91
43.5	673.28	626.10	508.83	462.89	768.99		410.85	365.86
44.5	670.01	621.68*	505.40	458.33	765.12		406.76	360.69
45.5	666.53	617.19*	501.79	453.68	761.20		402.56	355.42
46.5	662.90	612.66*	498.13	448.94	757.13		398.29	350.02
47.5	659.41*	607.84*	494.41	444.09	752.97		393.86	344.54
48.5	655.60*	602.97*	490.54	439.13	748.69		389.32	338.93
49.5	651.65*	598.11*	486.60	434.11	744.33		384.69	333.22
50.5	647.94	593.17*	482.60	428.97	739.81		379.94	327.38
51.5	644.00*	588.22*	478.40	423.78	735.23		375.10	321.44
52.5	639.79*	583.00*	474.18	418.37	730.57		370.11	315.40
53.5	635.60	577.75*	469.91	413.06	725.77		365.04	309.24
54.5	631.44*		465.46	407.47	720.85		359.86	302.98
55.5	627.74*		460.92	401.96	715.83		354.54	296.59
56.5			456.31	396.26	710.67		349.12	290.12
57.5			451.64	390.47	705.52		343.60	283.50
58.5	613.48*		446.85	384.64	700.24		337.98	276.80
59.5	609.21*		441.90	378.66	694.71		332.22	269.77
60.5	604.26*		436.97	372.60	688.56		326.34	263.06
61.5			431.86	366.44	682.12		320.37	256.01
62.5			426.64	360.18	677.82		314.30	248.85
63.5			421.46	353.83	671.96		308.11	241.59
64.5			416.08	347.47	665.98		301.82	234.24
65.5			410.63	340.98	659.91		295.39	226.74
66.5			405.12	334.40	653.75		288.87	219.16
67.5	589.42*				647.46		282.21	211.45
68.5					641.09		275.49	203.64
69.5					634.60		268.63	
70.5					628.03		261.67	
71.5					621.31		254.58	
72.5					614.51		247.40	
73.5					607.60		240.10	
74.5					600.60		232.69	
75.5					593.46		225.17	
76.5					586.28		217.54	
77.5					578.96		209.82	
78.5					571.54		201.93	
79.5					564.06*			
80.5					556.40*			
81.5					548.48*			
82.5					540.85*			
83.5					532.83*			
84.5					524.70*			
85.5					516.47*			
86.5					508.23*			
87.5					499.74*			
88.5					491.49*			
89.5					482.85*			

*Denotes overlapped line.

TABLE II
Band heads and band origins for IO

(v', v'')	ν_0, cm^{-1}	Band head, Å in air		λ_{Head} (obs. - calc.), Å	
		Coleman, Gaydon, and Vaidya	Our measurements	Coleman, Gaydon, and Vaidya	Our measurements
(5,0)		4189.0		3.0	
(4,0)		4268.2*		0.1	
(3,0)	22951.52	4355.9	4355.59	0.3	0.05
(4,1)		4396.7		2.4	
(2,0)	22470.07	4448.7	4448.87	-0.2	0.02
(3,1)		4487.7	4487.17	0.6	0.10
(1,0)		4548.1		-0.5	
(2,1)		4586.7	4586.16	0.5	0.01
(3,2)		4624.9		0.0	
(4,3)		4668.3		3.5	
(1,1)		4693.5		1.3	
(2,2)	21133.11	4731.2	4730.29	1.0	0.01
(3,3)		4763.3		-6.2	
(0,1)		4806.1	4805.73†	0.4	0.02
(1,2)		4844.5		1.4	
(3,4)		4920.9	4921.36	-0.4	0.04
(0,2)	20137.11	4963.6	4964.23	-0.6	0.04
(1,3)		5002.3		0.4	
(2,4)		5049.8	5040.76†	9.0	0.00
(0,3)	19481.63	5131.0	5131.21	-0.1	0.05
(2,5)		5208.8	5208.52†	0.6	0.33
(3,6)		5248.7		0.3	
(0,4)	18835.25	5307.5	5307.27	0.2	0.02
(1,5)		5345		-0.3	
(2,6)		5385.5	5384.45	1.0	-0.01
(3,7)		5422		-2.8	
(0,5)		5495	5493.18	1.8	0.01
(1,6)		5533		1.8	
(4,9)		5655.5		3.4	
(0,6)	17569.10	5692	5689.67	2.3	0.01
(1,7)		5730		2.5	
(2,8)		5767	5766.35†	0.6	-0.06
(0,7)		5900		2.4	
(1,8)		5939		4.0	
(2,9)	16734.46	5976	5973.37	2.6	0.02
(1,9)		6152.5		-2.0	
(2,10)		6193	6192.18†	0.7	-0.22
(3,11)		6231.5		0.3	
(4,12)		6273		1.9	

*Coleman, Gaydon, and Vaidya quote 4286.2 Å which apparently is due to a misprint.

†Overlapped.

2. Determination of ν_0 , $(B' - B'')$ and $(D' - D'')$

The band origins ν_0 were determined from the equation

$$(1) \quad R(J-1) + P(J) = 2\nu_0 + 2(B'_v - B''_v)J^2 - 2(D'_v - D''_v)J^2(J^2 + 1)$$

by plotting $R(J-1) + P(J) - 2(B'_v - B''_v)J^2$ against J^2 , using approximate values of $(B'_v - B''_v)$, and extrapolating to $J = 0$. The values obtained are given in Table II. More accurate values for the differences $(B'_v - B''_v)$ and $(D'_v - D''_v)$ were next determined by plotting $[R(J-1) + P(J) - 2\nu_0]/2J^2$ against $(J^2 + 1)$. These values were then combined with the B and D values determined in Section 1, to obtain B and D values for the other vibrational levels. The rotational constants obtained in this manner are given in Table III.

TABLE III
Rotational constants for IO
A. Upper $^2\Pi_{3/2}$ state

v'	Bands	B_v , cm^{-1} (measured)	D_v , cm^{-1} (measured)	B_v , cm^{-1} (calculated)
0	(0,2) (0,3) (0,4) (0,6)	0.27491	0.33×10^{-6}	0.27498
2	(2,0) (2,2) (2,9)	0.26974	0.35	0.26952
3	(3,0)	0.26665	0.38	0.26679

B. Lower $^2\Pi_{3/2}$ state

v''	Bands	B_v , cm^{-1} (measured)	D_v , cm^{-1} (measured)	B_v , cm^{-1} (calculated)
0	(2,0) (3,0)	0.33890	0.36×10^{-6}	0.33891
2	(0,2) (2,2)	0.33347	0.36	0.33346
3	(0,3)	0.33068	0.36	0.33070
4	(0,4)	0.32794	0.36	0.32793
6	(0,6)	0.32234	0.36	0.32233
9	(2,9)	0.31377	0.37	0.31377

3. Determination of ΔG , $(B_{v_1} - B_{v_2})$, and $(D_{v_1} - D_{v_2})$

To provide a check on the molecular constants derived in Sections 1 and 2 the quantities ΔG , $(B_{v_1} - B_{v_2})$, and $(D_{v_1} - D_{v_2})$ were determined from the appropriate combination relations between corresponding lines of pairs of bands having one state in common (Herzberg 1950, p. 188). The evaluation of these quantities was carried out in two stages in a manner similar to that discussed in Section 2. First, approximate values of $(B_{v_1} - B_{v_2})$ were assumed and the data used to determine accurate values of ΔG . Second, these values of ΔG were combined with the experimental data to determine more accurate values for $(B_{v_1} - B_{v_2})$ and $(D_{v_1} - D_{v_2})$. The values of ΔG , $(B_{v_1} - B_{v_2})$ and $(D_{v_1} - D_{v_2})$ were found to be in good agreement with those derived by method 2.

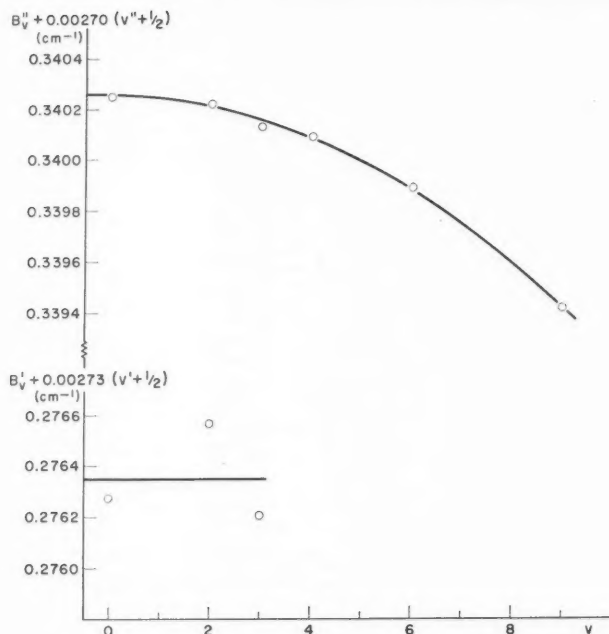
4. Determination of B_e , D_e , α_e , γ_e , and r_e

The variation of B with v for the upper and lower states is shown in Fig. 3. For the lower state a marked curvature is observed, but the variation is very regular and it was found that the B values could be fitted to the quadratic equation

$$(2) \quad B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2$$

to within $\pm 0.00002 \text{ cm}^{-1}$. Final values for B_e , α_e , and γ_e were determined by the method of least squares and are given in Table IV. The values of B_e calculated from these constants are given in Table III.

For the upper state it is apparent that one or more of the B values is perturbed. This is perhaps not surprising in view of the predissociations observed near $v' = 1$ and $v' = 4$. Since the magnitudes of the perturbations are not known, a linear dependence of B on v was assumed and values for B_e and α_e were determined by the method of least squares. The constants are given in Table IV and the calculated values for B_e are given in Table III. It may be

FIG. 3. Variation of B with v for the ground and excited states of IO.

noted that while the theoretical value of α , calculated assuming a Morse potential function (Herzberg 1950, p. 108) and our final molecular constants (Table IV), agrees well with the experimental values for the lower state ($\alpha'_{\text{calc}} = 0.00260 \text{ cm}^{-1}$, $\alpha'_{\text{obs}} = 0.00269_6 \text{ cm}^{-1}$), the agreement is less satisfactory for the upper state ($\alpha'_{\text{calc}} = 0.00309 \text{ cm}^{-1}$, $\alpha'_{\text{obs}} = 0.0027_3 \text{ cm}^{-1}$).

TABLE IV
Molecular constants for IO

$X^2\Pi_{3/2}$	$A^2\Pi_{3/2}$
$B_e = 0.34026 \text{ cm}^{-1}$	$B_e = 0.2763_8 \text{ cm}^{-1}$
$\alpha_e = 0.00269_6 \text{ cm}^{-1}$	$\alpha_e = 0.0027_3 \text{ cm}^{-1}$
$\gamma_e = -0.000009_7 \text{ cm}^{-1}$	$D_e = 0.32 \times 10^{-6} \text{ cm}^{-1}$
$D_e = 0.36 \times 10^{-6} \text{ cm}^{-1}$	$r_e = 2.072_3 \text{ \AA}$
$r_e = 1.8676 \text{ \AA}$	$\omega_e = 514.5_7 \text{ cm}^{-1}$
$\omega_e = 681.4_7 \text{ cm}^{-1}$	$\omega_e x_e = 5.5_2 \text{ cm}^{-1}$
$\omega_e x_e = 4.2_9 \text{ cm}^{-1}$	$T_e = 21557.8_1 \text{ cm}^{-1}$
$\omega_e y_e = -0.01_3 \text{ cm}^{-1}$	

From the graphical procedures used in Section 3, it was found that the D values for the lower state showed a very slight increase with increasing v . The magnitude of this effect was comparable to the accuracy of the measurements, hence no accurate value for β'' could be determined experimentally. Theoretically, the value of β'' derived from our final molecular constants and the

equation given by Herzberg (1950, p. 108) is $\beta'' = 0.002 \times 10^{-6} \text{ cm}^{-1}$. Combining this value with the D'' values given in Table III we obtain $D''_e = 0.36 \times 10^{-6} \text{ cm}^{-1}$. For the upper state the values of $(D''_1 - D''_2)$ cannot be considered as highly significant owing to the perturbations present. The theoretical value for β' is $0.009 \times 10^{-6} \text{ cm}^{-1}$. Combining this value with the D' values given in Table III we obtain $D'_e = 0.32 \times 10^{-6} \text{ cm}^{-1}$ (see Table IV). The experimental values of D''_e and D'_e are in good agreement with the values calculated from the equation $D_e = 4B_e^3/\omega_e^2$, viz. $D''_{\text{calc}} = 0.339 \times 10^{-6} \text{ cm}^{-1}$, $D'_{\text{calc}} = 0.319 \times 10^{-6} \text{ cm}^{-1}$.

Values for r_e were calculated from the equation $r_e^2 (\text{\AA}^2) = 16.8630/\mu B_e$ where μ is the reduced mass of the IO molecule in atomic mass units ($I = 126.9453$, $O = 16.0000$). The values are given in Table IV.

5. Determination of ω_e , $\omega_e x_e$, $\omega_e y_e$, and T_e

The vibrational constants for the upper and lower states and the electronic term value T_e for the excited state were determined by fitting the band origins given in Table II to the equation

$$(3) \quad \nu_0 = T_e + \omega'_e(v + \frac{1}{2}) - \omega'_e x'_e(v + \frac{1}{2})^2 - [\omega''_e(v + \frac{1}{2}) - \omega''_e x''_e(v + \frac{1}{2})^2 + \omega''_e y''_e(v + \frac{1}{2})^3].$$

Only two vibrational constants could be derived for the excited state owing to the limited data available; for the lower state it was found that a cubic expansion fitted the data to within the experimental error. The constants were obtained by the method of least squares and are given in Table IV.

DISCUSSION

From the rotational analysis of the bands it is clear that the carrier must be a diatomic or a linear polyatomic molecule. Since the bands have been observed in absorption during the flash photolysis of mixtures of iodine and oxygen, the carrier can only contain one or both of these elements. The only possibility, consistent with the rotational constants, is IO and it is interesting to note that the ground-state bond length obtained on the basis of this conclusion is consistent with the ground-state bond lengths of related molecules. Thus $r_0(\text{IO}) - r_0(\text{ClO}) = 0.325 \text{ \AA}$ is in good agreement with $\frac{1}{2}[r_0(\text{I}_2) - r_0(\text{Cl}_2)] = 0.338 \text{ \AA}$ and $r_0(\text{HI}) - r_0(\text{HCl}) = 0.331 \text{ \AA}$ (Herzberg 1950). It should be pointed out that the alternative carrier proposed by Vaidya (1937), viz. Cl, cannot be eliminated on the basis of the rotational analysis alone. This possibility is excluded, however, by the flash photolysis experiments and the observation by Coleman, Gaydon, and Vaidya of the bands in emission from an oxyhydrogen flame to which iodine is added.

Our results confirm the vibrational assignments of Coleman, Gaydon, and Vaidya. The wavelengths of the band heads calculated from our final molecular constants are found to be in satisfactory agreement with the measured values (see Table II). The vibrational constants of the ground and excited states are now known with greater precision, but it is not possible to improve significantly the earlier estimates for the dissociation energy since considerable extrapolations are needed for both states. The values quoted by Coleman, Gaydon, and

Vaidya (1948) and by Durie and Ramsay (1958) are $D''_0 = 44$ kcal/mole and 42 ± 5 kcal/mole respectively.

It is interesting to note that several diffuse bands were observed in emission from the flame source used even under conditions of high-resolving power. This result is in marked contrast to the general absence of such bands in emission from discharge tube sources. The appearance of diffuse bands from flame sources may be attributed to the higher pressures prevalent in flames and to the fact that conditions in hydrogen diffusion flames approximate to thermal equilibrium (Durie 1952; Gaydon and Wolfhard 1953).

REFERENCES

- COLEMAN, E. H., GAYDON, A. G., and VAIDYA, W. M. 1948. *Nature*, **162**, 108.
DURIE, R. A. 1952. *Proc. Phys. Soc. A*, **65**, 125.
DURIE, R. A. and RAMSAY, D. A. 1958. *Can. J. Phys.* **36**, 35.
EDLÉN, B. 1953. *J. Opt. Soc. Am.* **43**, 339.
GAYDON, A. G. and WOLFARD, H. G. 1953. *Flames, their structure, radiation, and temperature* (Chapman & Hall, Ltd., London), p. 142.
HARRISON, G. R. 1939. *M.I.T. wavelength tables* (John Wiley & Sons, Inc., New York).
HENZBERG, G. 1950. *Spectra of diatomic molecules* (D. Van Nostrand Co., Inc., Princeton, N.J.).
TOMKINS, F. S. and FRED, M. 1951. *J. Opt. Soc. Am.* **41**, 641.
VAIDYA, W. M. 1937. *Proc. Indian Acad. Sci. A*, **6**, 122.

AN ANALYSIS OF A SPECTROGRAM OF THE RED AURORA OF FEBRUARY 10/11, 1958, IN THE WAVELENGTH RANGE 7300-8700 Å¹

A. VALLANCE JONES

ABSTRACT

A high-dispersion photographic infrared spectrum covering the 7300-8700 Å region was obtained from the great red aurora of February 10/11, 1958. This spectrum shows the $\lambda\lambda 7774$ and 8446 OI lines to have been enhanced at least five times relative to normal aurora. The most striking feature of the spectrum was the appearance with high intensity of the forbidden $^2D-^2P$ multiplet of OII. The measured wavelengths and relative intensities of the features of the spectrum are listed.

1. INTRODUCTION

The great type-A red aurora of February 10/11, 1958, was observed simultaneously over a very wide geographical area. Spectra of the display have been obtained in Alaska by Belon and Clark (1959), at Yerkes Observatory by Wallace (1959), and near Moscow by Mironov, Prokudina, and Shefov (1959). At Saskatoon, a high-dispersion spectrogram was obtained in the region 7300-8700 Å. In addition, a set of nine low-dispersion (330 Å/mm) spectra (over the range 3750-7000 Å) were obtained with a Perkin-Elmer patrol spectrograph. In common with the results obtained by other investigators, these spectra show unusual enhancements of some atomic lines of oxygen and nitrogen. In particular the infrared spectrum shows the forbidden [OII] $^2D-^2P$ doublet with very high relative intensity. The presence of this feature was tentatively assumed by Omholt (1957) in low-dispersion spectra obtained from the higher-altitude portions of auroral forms. Dufay (1959) obtained further evidence of its appearance by just resolving the doublet in a photo-electric spectrum of a low-latitude aurora. Wallace (1959) provided very good evidence for the appearance of the doublet in a high-dispersion spectrum obtained at Yerkes Observatory on December 5, 1958; in his spectrum the lines appear superposed on the almost coincident $P_1(1)$ and $P_2(2)$ lines of the underlying (8-3) OH night airglow band. While the spectra of Dufay and Wallace leave little doubt of the identification of the multiplet, the spectrum obtained at Saskatoon puts the matter beyond question since the lines of the doublet are completely separated and the night airglow lines are absent.

2. EXPERIMENTAL

The infrared auroral spectrum was obtained with a dispersion of 66 Å/mm in the first order of the 9-in. $f/0.8$ auroral spectrograph at Saskatoon. The spectral slit width was 5.4 Å. A Kodak spectroscopic I-N plate, hypersensitized

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in an ammonia-ethanol bath, was used. A Wratten 23 filter eliminated the second- and third-order spectra. The plate was exposed to the red aurora of February 10/11 for 9 hours 40 minutes, between 1820 and 0420 hours Mountain Standard Time. The plate remained in the spectrograph and subsequently received a further 5-hour 53-minute exposure to aurora over a period lasting until February 23. Some of this later aurora was also type-A red aurora; from past experience with this spectrograph it is believed that the spectrum obtained is almost entirely to be attributed to the very intense display of February 10/11.

A print of the spectrogram is reproduced in Fig. 1 together with a night

TABLE I
Wavelengths and relative intensities of auroral features 7300-8700 Å

Feature	Observed wavelength	Laboratory wavelength	Relative peak intensity		
			Feb. 10/11 aurora	Normal aurora (Meinel)	Normal aurora (Saskatoon)
OII, (2F) $2\frac{1}{2}$ - $1\frac{1}{2}$	7319.7	7319.4	17.0	0	0
$1\frac{1}{2}$ - $\frac{1}{2}$, $1\frac{1}{2}$ - $1\frac{1}{2}$	7330.1	7330.0	11.8	0	0
N_2 , 1P (5-3)	7341.6				
	7350.1				
	7360.7				
	7373.0				
	7384.2		2.7	1.5	
	7466.6		8.9	5.1	9
N_2 , 1P (4-2)	7480.1				
	7490.0				
	7503.1		8.5	4.6	9
	7586.9		9.0	6.7	9.2
N_2 , 1P (3-1)	7619.6				
	7625.8				
O_2 (atmos.)					
(1-1) R-branch	7687.1		27	12	20
N_2 , 1P (2-0)	7703.1				
	7713.2				
	7726.9				
	7738.5				
	7751.7		10.9	8.6	14
	7773.7	7773.4	>100	8.2	13
OI, (1)	7826.9		8.9	8.8	11
N_2^+ , Meinel, (2-0)	7860.8		7.6	8.2	8.6
	7875.9		9.7	13	19
N_2^+ , 2-0?	7913.6				
OI, (19)	7994.8	7995.1	3.1	1.3	2.6
	8054.7		4.6	4.6	4.6
N_2^+ , Meinel, (3-1)	8090.8				
	8105.9		4.8	6.5	7.2
	8185.9	8186.6	2.7	1.3	1.4
NI , (2) ($1\frac{1}{2}$ - $2\frac{1}{2}$) ($\frac{1}{2}$ - $1\frac{1}{2}$)	8216.4	8216.3	4.2	1.9	2.8
NI , (2) ($2\frac{1}{2}$ - $2\frac{1}{2}$)	8241.9		v.w.		
Unidentified feature	8296.6		v.w.	1.0	
N^+ , Meinel (4-2)	8346.0		v.w.	1.7	
	8399.2	8399.7	v.w.		
OH, 6-2, $P_1(2)?$	8411.8		3.0		
Unidentified	8423.2		v.w.		
OH, 6-2 $P_1(3)?$	8429.6	8430.7	v.w.		
OI, (4)	8446.2	8446.5	>100	12	17
O_2 , atmos. (0-1) R-max.	8628.6		3.7	23	27
Origin	8642.9				
P-max.	8656.4				

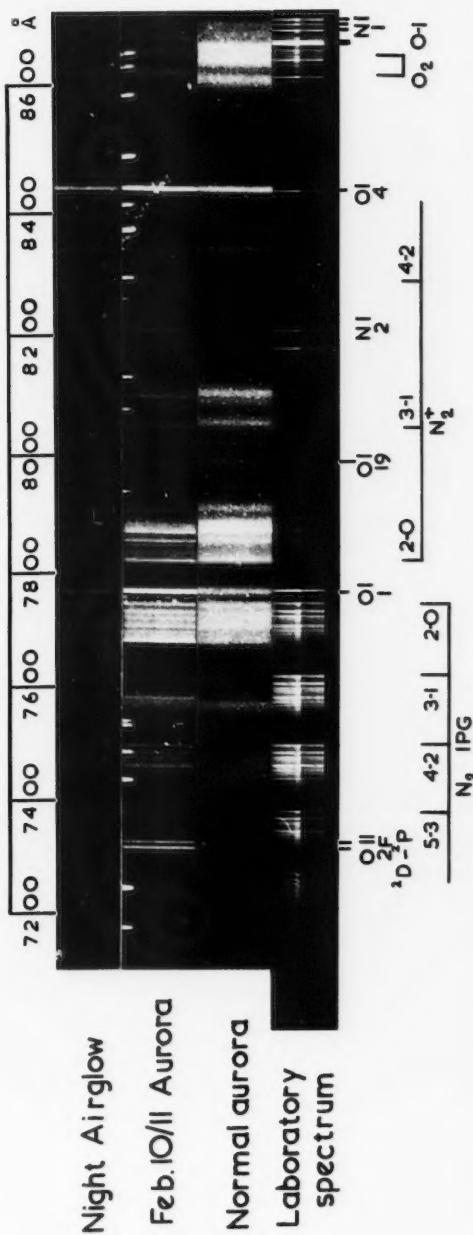
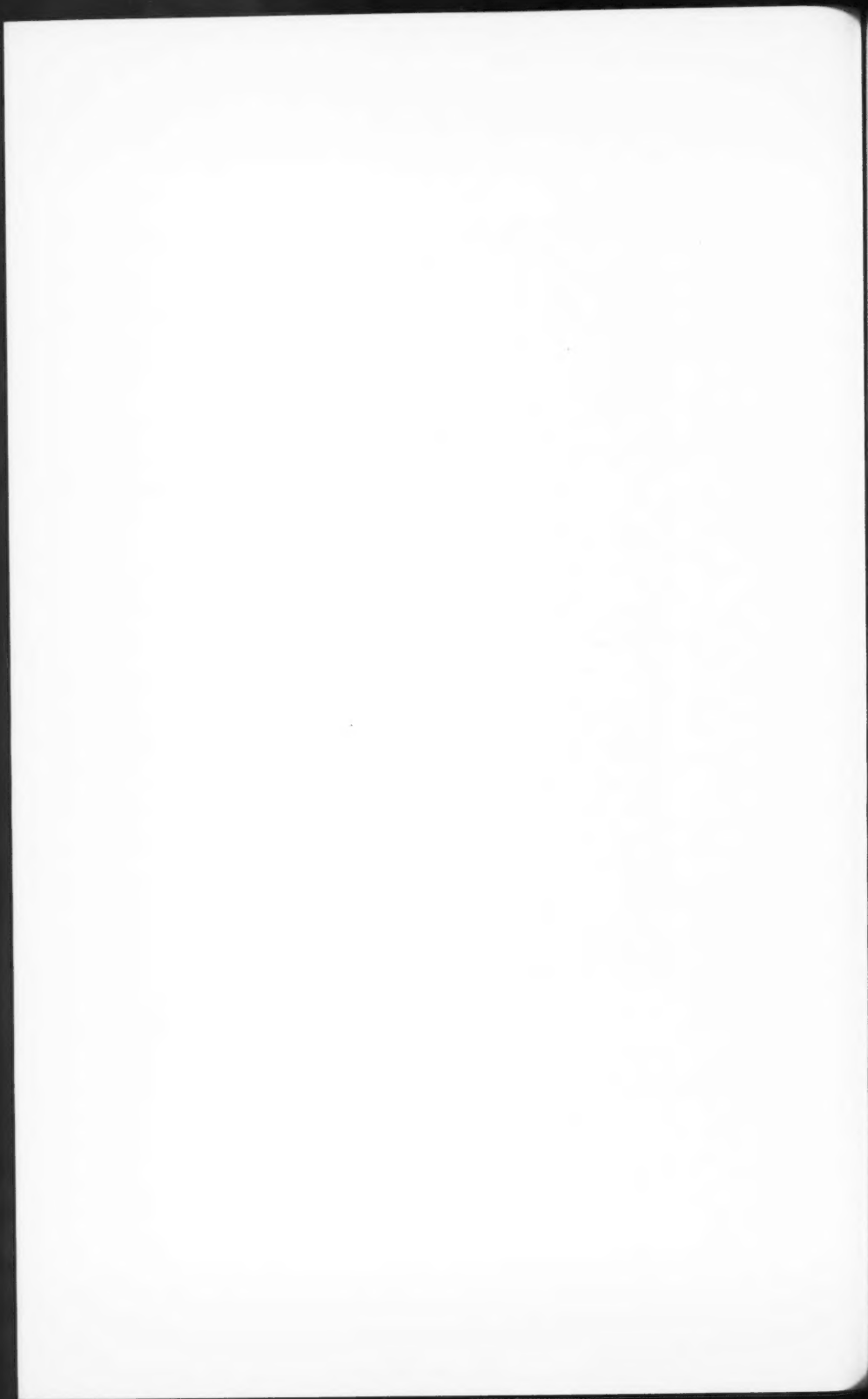


FIG. 1. Spectra in 7200-8700 Å region of night airglow, February 10-11 type-A red aurora, normal aurora (October 19, 1953), and a N_2 -hollow-cathode discharge. The night airglow spectrum is slightly contaminated by aurora.



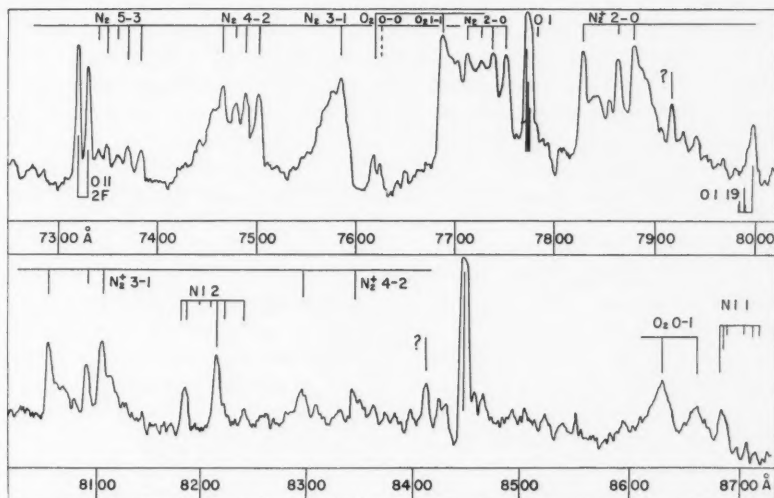


FIG. 2. Microphotometer tracing of the February 10/11 red aurora spectrum. The positions of the principal molecular bands and atomic multiplets are indicated. The atomic multiplets are identified by the numbers adopted by Moore (1945) and by Chamberlain and Oliver (1953).

airglow spectrum obtained with a 45-hour exposure on the same plate. For comparison, a spectrum of normal aurora obtained at Saskatoon with a spectrograph of dispersion 132 Å/mm and spectral slit width 9.3 Å is reproduced in the same figure. The fourth spectrum in Fig. 1 is that obtained from a N_2 hollow-cathode discharge, with a spectrograph of still higher dispersion (20 Å/mm).

The wavelengths of the features of the auroral spectrogram were measured by setting up an interpolation based on the Ne comparison spectrum superposed on the auroral spectrum. Unfortunately, the wavelengths of the principal atomic features obtained in this way showed a systematic difference of $1.4 \pm 0.6 \text{ Å}$ from the accepted laboratory values. This was attributed to the fact that the comparison spectrum was not applied until the plate was about to be removed from the spectrograph 12 days after the principal auroral exposure; it can only be supposed that some slight mechanical shock or thermal effect led to the observed shift. The final wavelengths, corrected for this displacement, are listed in Table I. The wavelengths should be accurate within $\pm 0.6 \text{ Å}$.

The relative peak intensities of some of the features listed in Table I were calculated with the help of an intensity calibration photographed on the same plate. This calibration was produced by exposing the spectrograph to a low-brightness source (Shepherd 1954), with a rotating step sector at the slit. The low-brightness source was calibrated against a black-body standard. The relative intensities so obtained are set out in column 4 of Table I.

These relative intensities may be compared with those listed by Meinel (1951) whose values are listed in column 5 of Table I. The spectral slit width employed by Meinel seems to have been about 12 to 15 Å compared with about 5 to 6 Å for the present study. Consequently, in his spectrum, lines and sharp band heads may appear weaker by a factor of up to 2.5 in comparison with unresolved bands and continuum.

A further comparison may be made with the relative brightnesses listed in column 6 of Table I. These values were obtained from a normal auroral display observed from Saskatoon during the night of April 5/6, 1957. The spectrum was photographed with a 5-in. $f/0.8$ spectrograph (Petrie and Small 1952) on a I-N plate. The plate was developed together with a similar plate on which an intensity calibration had been applied as described above. The spectral slit width for this exposure was about 9.3 Å. For this spectrum, the relative intensities of the features do not differ significantly from the values reported by Meinel.

3. GENERAL FEATURES OF SPECTRUM

In comparison with the spectrum of normal aurora the most striking points are:

(i) The $\lambda\lambda 7774$ and 8446 OI multiplets belonging to the $3s-3p$ transition array are from 5 to 10 times more intense relative to the N_2^+ bands than in normal low-level aurora.

(ii) The $3p^3P-3s'^3D^0$, OI, multiplet (19)* is definitely present; its relative intensity may be slightly enhanced in comparison with normal aurora.

(iii) The $3s^4P-3p^4P^0$, NI, multiplet (2) is present with a somewhat enhanced intensity relative to the normal auroral spectrum.

(iv) The relative intensities of the first positive N_2 bands and the Meinel N_2^+ bands do not seem much different.

(v) The $^2D-^2P$, OII, multiplet (2F) lines are present with extraordinary intensity. The measured wavelengths agree to within 0.3 Å with the theoretical values. The intensity ratio between the lines was found to be 1.4. This is in fair agreement with the theoretical values of Seaton and Osterbrock (1957), who predict the range of values of ratio to be 1.24 to 1.31.

(vi) The 0-1 O_2 atmospheric band appears to be particularly weak in comparison with the N_2^+ bands. This is possibly due to the increased dispersion of the spectrograph. However, the spectral slit width of the 9-in. spectrograph is about half that of the lower-dispersion spectrograph while the relative intensity of the O_2 band is about 8 times less than for the normal auroral spectrum.

The sharp maximum at 7687.1 Å attributed by Chamberlain, Fan, and Meinel (1954) to the R -branch head of 1-1 O_2 band appears clearly. Strangely, its intensity relative to that of the neighboring 2-0 first positive N_2 band is not very different from its value in normal aurora; if anything its relative intensity is greater. This observation might appear to raise some doubt as to the correctness of the identification of the 7687 -Å peak; however, it must be borne in

*The multiplet numbers are those adopted by Moore (1945); see also Chamberlain and Oliver (1953).

mind that the sharp head of the 1-1 band would be less affected by the reduction in spectral slit width than the headless branches of the 0-1 band. Moreover, the rapid drop in emulsion sensitivity beyond 8600 Å makes the intensity calibration liable to considerable error in the region of the 0-1 band.

A comparison between the auroral and the laboratory spectra in Fig. 1 shows that all the measured intensity maxima within the N_2 and N_2^+ bands correspond to heads or lines occurring in the laboratory spectrum. The maximum at 7687.1 Å in the auroral spectrum does not, of course, appear in the laboratory spectrum.

There are a few unidentified features listed in Table I. The most intense is the line-like emission at 8411.8 Å. This is not an OH night airglow line as may be seen by comparing the auroral and night airglow spectra in Fig. 1.

4. CONCLUSIONS

The most striking feature of the spectrum of the February 10/11 red aurora in this spectral region was the great enhancement of the forbidden $^2D-^2P$ multiplet of OII. This observation may be an important one in an understanding of the mechanism of type-A red aurora. The enhancement of this multiplet is very beautifully paralleled by the enhancement of the related $^2D-^4S$ multiplet at $\lambda\lambda 3729-3726$ observed by Wallace for the same aurora. The intensification of these transitions may very well be a height effect.

The other notable peculiarity of this spectrum is the generally enhanced relative brightnesses of its atomic lines in comparison with those of the molecular bands. This effect, which has been noted by other observers for the same aurora, is probably also a height effect.

ACKNOWLEDGMENTS

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REFERENCES

- BELON, A. E. and CLARK, K. C. 1959. *J. Atmospheric and Terrest. Phys.* **16**, 220.
- CHAMBERLAIN, J. W., FAN, C. Y., and MEINEL, A. B. 1954. *Astrophys. J.* **120**, 560.
- CHAMBERLAIN, J. W. and OLIVER, N. J. 1953. *J. Geophys. Research*, **58**, 457.
- DUFAY, M. 1959. *Ann. géophys.* **15**, 134.
- MEINEL, A. B. 1951. *Astrophys. J.* **113**, 583.
- MIRONOV, A. V., PROKUDINA, V. S., and SHEFOV, N. N. 1959. Spectral, electrophotometrical and radar researches of aurora and airglow (Academy of Sciences, Moscow).
- MOORE, C. E. 1945. A multiplet table of astrophysical interest. Contribution No. 20 from the Princeton University Observatory.
- OMHOLT, A. 1957. *J. Atmospheric and Terrest. Phys.* **10**, 320.
- PETRIE, W. and SMALL, R. 1952. *Astrophys. J.* **116**, 433.
- SEATON, M. J. and OSTERBROCK, E. E. 1957. *Astrophys. J.* **125**, 66.
- SHEPHERD, G. G. 1954. Scientific Report No. AR-16, Contract AF 19(122)-152, University of Saskatchewan, Saskatoon, Saskatchewan.
- WALLACE, L. 1959. *J. Atmospheric and Terrest. Phys.* **17**, 46.

ROTATIONAL AND VIBRATIONAL INTENSITY DISTRIBUTION OF THE FIRST NEGATIVE N_2^+ BANDS IN SUNLIT AURORAL RAYS¹

A. VALLANCE JONES AND D. M. HUNTEN

ABSTRACT

Spectra of sunlit auroral rays were obtained from Saskatoon during the auroras of September 3/4 and 4/5, 1958. The resolution of these spectra was sufficiently high to enable measurements to be made of the relative intensities of the lines of the 0-0 first negative N_2^+ band as well as the relative intensities of bands of the $\Delta v = -1$ sequence of this system. An analysis of the rotational line intensities shows they are consistent with an excitation process in which N_2^+ ions in thermal equilibrium with the atmosphere at 2200° K fluoresce under the influence of solar radiation. The vibrational intensity distribution also is consistent with a fluorescent excitation from a state of thermal equilibrium at about 2050° K. It is shown that the results are not consistent with a fluorescent excitation process in which the rotational and vibrational degrees of freedom of the N_2^+ ions come into radiative equilibrium with the solar radiation. Earlier conclusions that radiative equilibrium did hold for vibration are shown to be in error as a result of the high rotational temperature and the low dispersion used. It is concluded that the destruction of N_2^+ ions as a result of dissociative recombination proceeds sufficiently fast to prevent any significant approach to radiative equilibrium. This investigation provides a strong indication that the kinetic temperature of a sunlit auroral ray (perhaps in the 400-500 km region) is in the neighborhood of 2000° K. This may be somewhat higher than the temperature of the normal atmosphere at this height.

1. INTRODUCTION

One of the principal objectives of the study of aurora is the determination of the properties of the upper atmosphere. The emission from the most common forms of aurora is concentrated between 80 and 120 km. While the summits of some auroral rays may occasionally reach as high as 600 km the work of Störmer (1955) has shown that the forms occurring at the greatest heights are the sunlit auroral rays. The highest measured points for these rays lie near 1100 km while the lower ends are generally found between 200 and 400 km. Consequently, spectroscopic observations of sunlit aurora should enable information to be obtained about conditions in the 400 to 600 km height range.

Spectra of sunlit rays have been obtained by Störmer (1939). These spectra which were obtained from parts of the rays at heights between 400 and 650 km showed the first negative N_2^+ bands to be particularly strong and to exhibit an unusually great development of the vibrational sequences.

These results were interpreted by Bates (1949a) in a classic paper in which it was shown that the experimental data were consistent with the excitation by sunlight of N_2^+ by a resonance fluorescence process in which a special equilibrium distribution was set up among the vibrational levels of the ion. This distribution reflects the tendency of the vibrational degree of freedom to come

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into radiative equilibrium with the solar black-body radiation. For N_2^+ such a steady state can arise for the case when collisions are unimportant since pure vibrational and rotational transitions are forbidden. Bates also calculated the population rates for fluorescent excitation of the upper state of N_2^+ for the case where the collision rate is high enough to maintain thermal equilibrium in the ground state. The results of the latter calculation did not seem to fit Störmer's data unless an atmospheric temperature of 5000°K was assumed; this temperature appeared to be too high even for a height of 650 km. However, in view of the high rotational temperatures reported for sunlit rays in the present work, it seems that Störmer's data require reinterpretation.

Swings (1949) pointed out that the rotational structure of sunlit aurora should exhibit irregularities of the same kind as were found in the spectra of comets by Swings (1941) and McKellar (1942). These irregularities were shown by Swings and McKellar to arise from the presence of Fraunhofer lines in the exciting solar continuum. The observation of such irregularities in the spectra of sunlit aurora would provide definite evidence for the operation of the fluorescent mechanism in the excitation of sunlit aurora.

On the nights of September 3/4 and 4/5, 1958, high- and medium-dispersion spectra were obtained at Saskatoon of sunlit auroral rays. The analysis of these spectra, to which this paper is devoted, shows definitely that the sunlit rays were excited by resonance fluorescence and provides strong evidence to support the view that the rotational degree of freedom of the N_2^+ ion remained in thermal equilibrium with the atmosphere at a temperature of approximately 2200°K . The observed vibrational intensities of the $\Delta v = -1$ sequence of bands also appear to be close to that which would result from fluorescent excitation of ions in the distribution for thermal equilibrium at approximately 2050°K . This differs significantly from the distribution which would result from equilibrium with the solar radiation, which corresponds approximately to a vibrational temperature of 4200°K .

2. OBSERVATIONS

Displays of aurora exhibiting sunlit auroral rays were observed from Saskatoon on September 3/4 and 4/5, 1958. These rays showed the greyish-blue color described by Störmer (1955) and at times exhibited the characteristic intensity minimum where the rays crossed the boundary between the sunlit and dark regions of the atmosphere. The spectrographs were directed towards the sunlit, upper parts of rays. The sunlit portions of the rays were recognized, in general, by their unusual color. The characteristics of the spectra obtained show that this procedure was successful.

Three separate plates were obtained from the sunlit aurora. Two of these plates (one on each evening) were obtained using the 5-in. $f/0.8$ spectrograph described by Petrie and Small (1952). This instrument has a linear dispersion of 40 \AA/mm . These two exposures were made on Kodak 103a-O plates and covered the regions $3500\text{--}3950\text{ \AA}$ and $3500\text{--}4280\text{ \AA}$ respectively. A third, higher-dispersion spectrum was obtained using a 9-in. $f/0.8$ spectrograph having a dispersion of 20 \AA/mm . This exposure covered the sunlit parts of the display on both September 3/4 and 4/5; the spectral region covered was $3400\text{--}4000\text{ \AA}$.

A reproduction of the 3914-Å N_2^+ band from the high-dispersion plate is shown in Fig. 1; a reproduction of the same band as obtained from a normal aurora is also shown. Microphotometer tracings of the band have been published in a preliminary report of our results (Huntten, Koenig, and Vallance Jones 1959). A reproduction of one of the lower-dispersion plates is shown in Fig. 2 together with a spectrum of aurora obtained after dark the same night (September 4/5, 1958). These two spectra were obtained using a step slit having 11 segments with widths ranging from 0.2 to 2.0 mm in geometrical progression. Such a slit provides a means of determining the characteristic curve of the emulsion from a region where the spectrum is continuous.

3. RESULTS

The rotational structure of the 0-0 N_2^+ band for the sunlit auroral spectrum in Fig. 1 clearly corresponds to a much higher rotational temperature than does the normal spectrum. The relative intensities of the lines of the R branch were derived from the microphotometer tracing with the help of an intensity calibration applied to another part of the auroral plate; this calibration was made by photographing the spectrum of a standard low-brightness source (Shepherd 1954) with a rotating step sector at the slit of the spectrograph. The relative intensities of the R branch lines obtained in this way must then be corrected by subtracting the contributions of the higher lines of the P branch which coincide almost exactly with the R branch lines. The correction was made by assuming that the P branch line would have the same intensity as the corresponding R branch line from the same K' level. The results are given in Table I.

As a first approximation the corrected R branch line intensities were then used to derive a rotational temperature according to the usual graphical method (Section 6) of plotting $\log(I/K')$ against $K'(K'+1)$. The B_0 value for the $X^2\Sigma_g^+$ state of N_2^+ was used in the relation between the slope of the plot and the rotational temperature. The temperature obtained was 2100° K. This result must be regarded as a preliminary one only since no account has been taken of the nature of the excitation mechanism. A more correct treatment is given in Section 6.

It is clear from Fig. 1 that irregular fluctuations are present in the line intensities of the R branch; such irregularities are to be expected for fluorescent excitation of the band system by sunlight.

As was found by Störmer (1939) the relative intensities of the vibrational bands of the first negative system of N_2^+ are also abnormal in the sunlit auroral spectrum. This is particularly evident for the 4278-Å ($\Delta v = -1$) sequence of bands as may be seen by comparing the two spectra reproduced in Fig. 2. Figure 3(a) shows an intensity plot of this region derived from the spectrum of Fig. 2. This intensity plot was obtained from a microphotometer tracing across the fourth step in the spectrum (counting from the strongest step). A characteristic curve for the plate was derived by scanning across the spectrum at 3775 Å and 4260 Å where the auroral spectrum is quasi-continuous. Near the edge of its field the spectrograph suffers from severe vignetting which was

PLATE I

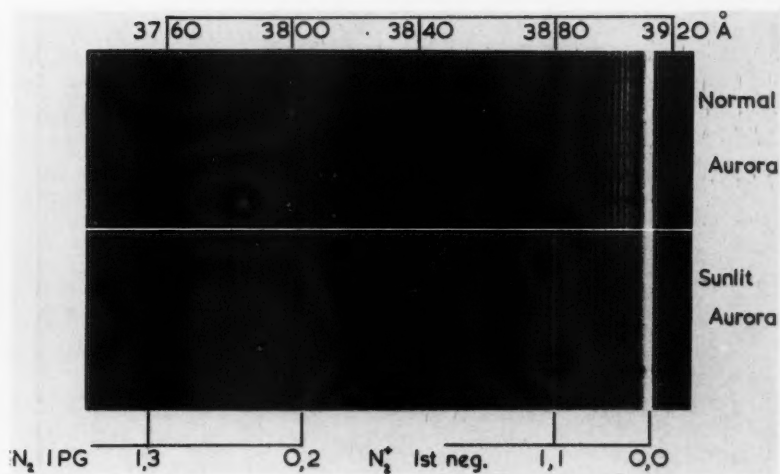


FIG. 1. The high-dispersion spectrum of sunlit aurora compared with that of a normal aurora later in the night; the rotational temperature of the former is much higher. The N_2 second positive bands are abnormally weak in the sunlit spectrum because they are not enhanced by resonance.

PLATE II

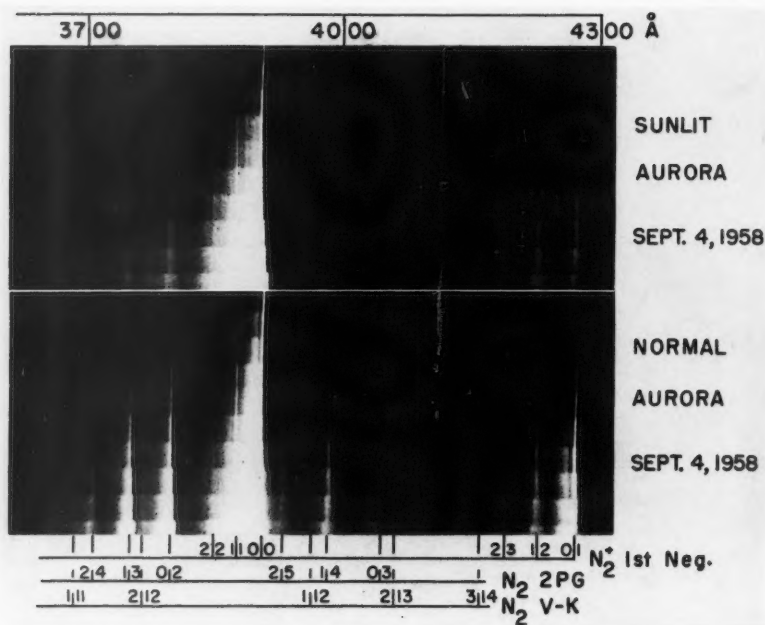


FIG. 2. The low-dispersion spectra of sunlit and normal aurora, taken with a step slit. The enhancement of the negative system with respect to the rest of the spectrum is again noticeable.

taken into account by calibrating the sensitivity of the instrument from 4200–4300 Å with the help of a low-brightness source. Figure 3 also shows a plot of the band sequence as obtained from the non-sunlit auroral spectrum of Fig. 2. In order to keep the peak density of the *P* branch of the 0–1 band within the range of accurate microphotometry the intensity plot for the non-sunlit aurora was derived from the seventh step of the spectrum. The consequent differences between the spectral slit widths for the two traces of Fig. 3

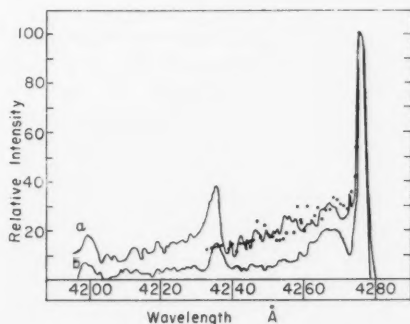


FIG. 3. (a) Intensity tracing of the 4278-Å group in the sunlit spectrum of Fig. 2. The dots show the synthetic spectrum for the 0–1 band at a rotational temperature of 2200° K. (b) A similar tracing for the normal auroral spectrum of Fig. 2.

will not seriously affect the measurements of the intensity ratios of the bands since the shapes of the bands are very similar. The vibrational sequence appears to be very much more strongly developed for the sunlit auroral spectrum. The significance of this result is considered further in the next section.

4. VIBRATIONAL INTENSITY DISTRIBUTION

Bates (1949a) has shown that the relative intensities of the 4278-Å (0–1), 4236-Å (1–2) and 4200-Å (2–3) first negative bands are of fundamental importance in the theoretical interpretation of the spectrum. The relative intensities required, however, cannot be taken directly from the curve of Fig. 3 because the high rotational temperature leads to overlapping of the bands. This effect is not very important for normal aurora but is of major significance in the case of the sunlit aurora which has been shown above to have a rotational structure corresponding to a temperature of over 2000° K. A similar difficulty in a more acute form was encountered by Clark and Belon (1959) in the analysis of somewhat lower-dispersion spectra of the $\Delta v = -2$ sequence of the bands.

The correction to the intensity of the 1–2 band was made by calculating a synthetic spectrum for the 0–1 band. The wavelengths of the rotational lines were taken from the data of Childs (1932). A value of 2200° K was adopted as an approximation to the rotational temperature. The synthetic spectrum was then derived for a spectral slit width of 4 Å by summing the contributions of all lines within a range of ± 2 Å of each wavelength at which the spectrum was

required. The synthetic spectrum was calculated at 4-Å intervals for the range 4236 Å–4284 Å. The 4-Å spectral slit width corresponds to the value for the segment of the slit which produced the spectrum from which the intensity plot of Fig. 3 was derived. This procedure supposes that the resolution function of the spectrograph was rectangular; in fact for this slit width it was found to be distinctly trapezoidal (as determined from the profile of the 4047-Å mercury line). As a consequence it is to be expected that the synthetic spectrum would tend to exhibit a somewhat "sharper" structure than the observed spectrum.

The synthetic spectrum so obtained is shown superimposed on the experimental curve in Fig. 3. The two curves fit well within the limits of experimental error set by the grain "noise" of the emulsion.

The relative intensities of the 0–1 and 1–2 bands may now be calculated on the assumption that the ratio will be equal to that of the peak intensities of the *P* branches after the contribution of the *R* branch of the 0–1 band has been subtracted. The result obtained is $I(0-1):I(1-2) = 100:26$. The result which would have been obtained if no correction had been made for the *R* branch contribution to the peak of the 1–2 band is 100:39. The ratio derived from the intensity trace for the non-sunlit aurora (where the correction is negligible) is 100:11. This agrees with the usual value of the ratio for normal aurora (Hunten 1955). For the sunlit aurora, the relative intensity of the third band (2–3) was estimated by extrapolating the background under its head as about 10; the full set of intensity ratios is thus 100:26:10.

To discuss the excitation mechanism we need the relative population rates $g(v')$ rather than the intensities. The relation between them is well known (Bates 1949*a*) and need not be repeated. It is no longer necessary to use Franck-Condon factors instead of relative transition probabilities in the calculation since a table of the latter has been given by Wallace and Nicholls (1955). The factors multiplying the relative intensities to convert them to relative population rates are then 0.93 for 1–2 and 1.06 for 2–3. We thus find $g(0):g(1):g(2) = 100:24:11$; the third is very uncertain. Reference to Bates' Table 12 (1949*a*) gives a vibrational "temperature" of about 2050° K. This "temperature" is not far from the rotational temperature 2200° K found in Section 6, and is certainly lower than the 4200° K given by Bates for the case of radiative equilibrium with sunlight.

5. THEORY OF THE ROTATIONAL ENERGY DISTRIBUTION

The work of Bates (1949*a*) on the vibrational intensity distribution showed that it could apparently be explained by assuming that the molecules are in equilibrium with the solar radiation. If it were not for the Fraunhofer lines in the sunlight, the molecules would have a vibrational temperature equal to the temperature of the sun's surface; Bates' result corresponds to a vibrational temperature of about 4200° K, suggesting that the Fraunhofer lines do have an appreciable effect. Since the N_2^+ molecule is homonuclear, it has no rotation-vibration nor pure rotational spectra; thus the only transitions governing the equilibrium are electronic. This effect is illustrated by McKellar's results

(1942) on comet spectra, in which the C_2 molecule gives a very high temperature while the CN gives a temperature about equal to that of the cometary gas (Swings 1943).

The new observations of sunlit auroral rays at high dispersion show what appears to be the analogous effect on the rotational energy distribution; although the temperature is lower, about $2100^\circ K$, this might be explained by the presence of Fraunhofer lines in the exciting sunlight. The spectrum to be expected on this mechanism was calculated and found indeed to be in fair agreement with the observations. However, it was thought best to calculate another spectrum on the assumption that the N_2^+ ground state had a Boltzmann distribution corresponding to the temperature of 2100° ; to our surprise, this gave much better agreement. The methods used will now be described; the two cases will be called "radiative equilibrium" and "thermal equilibrium".

A complete calculation for radiative equilibrium should take into account the absorption and emission by all the bands of the first negative and other systems, allowing for the intensity of the sunlight at each individual line. This would yield a new version of Bates' result for the vibrational distribution, as well as the rotational distribution of each rotational level of ground and excited states. However, it is not practical for several reasons: far too much work would be required; probably the wavelengths of all the lines have not been measured; and the theory would be almost impossibly complicated. Consideration was therefore restricted to the first negative system and the first two vibrational levels of each state; the 0-0 band (3914 \AA) is the most important, and the 0-1 band (4278 \AA) next. The 1-1 can be ignored because the transition probability is small, and the 1-0 because the solar continuum is much weaker in the ultraviolet (3582 \AA); moreover, these bands go to the level $v' = 1$ which does not directly concern us. Only two bands were thus included; the calculated spectrum may be expected to exaggerate the effects of individual Fraunhofer lines and allowance must be made for this in the comparison with observation.

Let us first consider the simple case in which only the levels $v' = 0$ and $v'' = 0$ are included. Figure 4(a) shows the rotational levels numbered with the quantum number K which is convenient to use when the spin splitting of each level can be neglected. Some of the possible transitions are indicated; it will be seen that there are two independent sets of levels since neither the absorbing nor the emitting transitions join them. The odd levels of the one state are in equilibrium with the even levels of the other. The equations describing the equilibrium may be set up with the aid of the principle of detailed balance: the probability of a transition and its inverse is proportional to the statistical weight of the final level. We use A and B to represent transition probabilities for emission and absorption, n for the population of a state, and I for the flux of radiation at the wavelength of a line. Then

$$A\nu^4 n'(K-1)(2K+1) = B\nu I_p n''(K)(2K-1)$$

and

$$A\nu^4 n'(K+1)(2K+1) = B\nu I_p n''(K)(2K+3).$$

The first of these expresses the fact that in equilibrium the number of transitions per unit time must be the same for both absorption and emission between an upper level numbered $K-1$ and a lower level numbered K ; this is a transition in the P branch and so the flux is called I_p . The second equation expresses the same fact for the R transition having the same lower level. Dividing the second equation by the first gives

$$(1) \quad \frac{n'(K+1)}{n'(K-1)} = \frac{2K+3}{2K-1} \frac{I_r}{I_p} = \frac{r(K)}{p(K)} = s(K).$$

The quantities p and r represent radiation fluxes multiplied by the statistical weight of the upper level concerned; their use will allow later equations to be written more compactly.

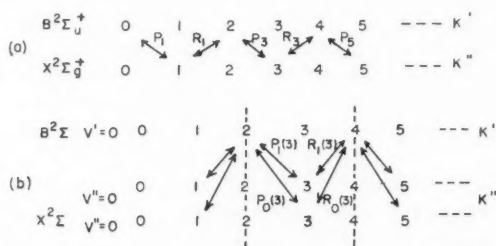


FIG. 4. (a) Rotational levels and transitions for part of the 0-0 band.

(b) The same, but including both 0-0 and 0-1 bands. (The vibrational numbers v'' of the X state should be 0 and 1, reading upwards.)

When we include the level $v'' = 1$ the situation becomes much more complicated; it is shown in Fig. 4(b). Because of the assumption of equilibrium it is possible to consider the transitions between the dotted lines by themselves. But within these lines there is now a loop, so that equilibrium is possible without having each absorption transition individually equal in rate to the corresponding emission. Instead, we must equate the number of transitions reaching each level to the number leaving; of the four equations thus found, one is redundant. Quantities relating to the 0-0 band will be given the subscript 0, and 1 will be used for the 0-1 band. The relative transition probabilities of these bands will be called q_0 and q_1 . The result will first be worked out for the specific levels shown in Fig. 4(b) and then generalized.

If $n''_0(3)$ is constant,

$$B\nu_0 q_0 n''_0(3) [p_0(3) + r_0(3)] = 7.1 \nu_0^4 q_0 [n'_0(2) + n'_0(4)];$$

no statistical weights appear on the left because they are included in the quantities p and r . For $n''_1(3)$ constant,

$$B\nu_1 q_1 n''_1(3) [p_1(3) + r_1(3)] = 7.1 \nu_1^4 q_1 [n'_0(2) + n'_0(4)].$$

Finally, for $n'_0(2)$ constant,

$$B\nu_0 q_0 n''_0(3) p_0(3) + B\nu_1 q_1 n''_1(3) p_1(3) = 7.1 n'_0(2) [q_0 \nu_0^4 + q_1 \nu_1^4].$$

If the first two equations are substituted in the third so as to eliminate the populations of the lower levels, the result is

$$\frac{n'_0(4)}{n'_0(2)} = \frac{q_0\nu_0^4r_0(3)[p_1(3)+r_1(3)]+q_1\nu_1^4r_1(3)[p_0(3)+r_0(3)]}{q_0\nu_0^4p_0(3)[p_1(3)+r_1(3)]+q_1\nu_1^4p_1(3)[p_0(3)+r_0(3)]}.$$

A more convenient form is obtained by dividing top and bottom by $q_0\nu_0^4p_0p_1$, using $s(K)$ as defined in (1) and writing q for $q_1\nu_1^4/q_0\nu_0^4$; at the same time we may replace the particular values of K by general ones:

$$(2) \quad \frac{n'(K+1)}{n'(K-1)} = \frac{s_0(K)[1+s_1(K)]+qs_1(K)[1+s_0(K)]}{[1+s_1(K)]+q[1+s_0(K)]}.$$

It is seen that (2) reduces to (1), as it should, if q is taken equal to zero. It is interesting to consider the special case in which the illuminating flux has a black-body spectrum; the ratio I_r/I_p depends on the wave-number difference of the R and P lines with the same K'' , and this is just the difference ΔF between the energy levels $K+1$ and $K-1$. From the definition of $s(K)$ in (1) it follows that

$$s_0(K) = s_1(K) = \frac{2K+3}{2K-1} \exp\left(-\Delta F \frac{hc}{kT}\right) = \frac{n'(K+1)}{n'(K-1)};$$

thus in this case the rotational temperature is equal to the temperature of the black body as would be expected from more general reasoning. The solar spectrum in the blue and ultraviolet deviates considerably from that of a black body; the detailed calculations show that the Fraunhofer lines happen to lie in such a way as to simulate a much lower temperature near 1200° K.

Equation (2) is not suitable for calculation for two reasons: first, its complexity, and second, because it gives only the ratio of adjacent odd or even levels and a large error could accumulate over the whole width of the band unless an unreasonable number of extra digits were carried. If (2) is examined it is seen to produce a weighted mean of s_0 and qs_1 , with the quantities in square brackets acting as weights. The value of the mean will not be greatly changed if all the weights are taken equal to 2; then we may write approximately

$$(3) \quad \frac{n'(K+1)}{n'(K-1)} \doteq \frac{s_0(K)+qs_1(K)}{1+q} \doteq 0.77s_0(K)+0.23s_1(K).$$

The numbers follow from the values of $q_0(0.54)$ and $q_1(0.23)$ given by Wallace and Nicholls (1955) and the definition of q just before equation (2). The radiation fluxes I_r and I_p may be found as fractions of the continuum from the Utrecht Atlas (Minnaert *et al.* 1940) and we will call their ratio $U(K)$; then

$$s_i(K) = \frac{2K+3}{2K-1} \frac{I_r}{I_p} = \frac{2K+3}{2K-1} U_i \exp\left(-\Delta F \frac{hc}{kT}\right),$$

where we have again used the Wien approximation to the black-body law. When these are substituted into (3) the Boltzmann factors are common; and

when a whole series of ratios as given by (3) is multiplied together, all the Boltzmann factors combine:

$$(4) \quad \frac{n'(K)}{n'(0)} = \prod_{m=2,4}^K [0.77U_0(m) + 0.23U_1(m)] (2K+1) \exp\left(-F \frac{hc}{kT}\right) \quad (\text{even levels}).$$

A similar expression holds for the ratio of odd levels to $K' = 1$. Build-up of error has now been eliminated from the Boltzmann factor but not from the term involving U ; thus, one must be careful in estimating the U 's from the Atlas and in making the calculations. F can be taken equal to $B''K(K+1)$.

The case of "thermal equilibrium" is much simpler. The question of what the molecules are in thermal equilibrium with will be considered later; for the present, the term will be taken to imply that the N_2^+ ground state has a Boltzmann distribution of the rotational levels, instead of a distribution determined by the radiative equilibrium as just discussed. This distribution will be

$$(5) \quad n''(K) = (2K+1) \exp\left(-B''K(K+1) \frac{hc}{kT}\right);$$

T no longer represents the temperature of the sun, but rather that of the ground-state distribution. If absorption of the 0-0 band alone is considered, the distribution in the upper state is

$$n'(K) = I_r(K-1)n''(K-1) + I_p(K+1)n''(K+1).$$

This will be altered very little if both the n'' are replaced by what is nearly their average, $n''(K)$; then

$$(6) \quad n'(K) \doteq (2K+1) \exp\left(-B''K(K+1) \frac{hc}{kT}\right) (I_r(K-1) + I_p(K+1)).$$

Throughout this development, normalizing constants have been omitted since only the distribution among levels is of interest. In (6), I_r and I_p can be taken as the fractional intensities u_r and u_p from the Utrecht Atlas with little error: the variation of the continuum cancels to first order since the P and R branches go in opposite directions. To second order, however, there is an appreciable variation in the mean wavelength of corresponding P and R lines; this is what causes the head in the P branch and the increasing spacing of the lines in the R branch. An approximate calculation of this effect showed that the measured temperature would be about 50° too low if it is 2100° K and the sun's color temperature 7150° K. This small correction is hardly significant in view of the other errors of measurement and interpretation, but it is included in our final result; it was not included in our preliminary announcement (Hunten, Koenig, and Vallance Jones 1959).

The 0-1 band can be included by adding to the last term of (6) the amount $q(I_r' + I_p')$ where the primed fluxes refer to this band. The fact that the first vibrational level is less populated than the zeroth is balanced by the greater solar flux at the longer wavelength; thus, only the ratio of the transition

probabilities enters as long as the vibration of the molecule is in radiative equilibrium. Actually, the vibration is somewhat less than this, but use of the full factor q will help to compensate the omission of other bands. Replacing the I 's by u 's as suggested above, we finally get from (6)

$$(7) \quad n'(K) \doteq (2K+1) \exp\left(-B''K(K+1) \frac{hc}{kT}\right) [u_r + u_p + q(u'_r + u'_p)].$$

In the next section the abbreviation \bar{u} is used for the quantity at the end of (7).

6. NUMERICAL CALCULATIONS AND RESULTS

The biggest part of the labor of calculation is the reading of the fractional intensity of sunlight at the position of each line of the 0-0 and 0-1 bands. As already mentioned, the solar spectrum used was that of the Utrecht Atlas, which gives intensity tracings on a large scale for the light from the center of the sun's disk. It would be better to have a spectrum of integrated sunlight, but this is much more difficult to obtain and is not available. The finite resolution of the spectrograph used to obtain the Atlas fills in the narrow lines appreciably; however, the lines for the whole sun must be somewhat filled in also because of the rotation and the resulting Doppler shift; thus, these two errors tend to cancel. The wavelengths of the N_2^+ lines are given by Childs (1932); they were marked lightly on the tracings of the Atlas and the fractional intensities estimated as closely as possible. Because the Fraunhofer lines are often narrow and the rotational lines may fall on their steep sides, some of these results are rather uncertain, perhaps by 5 or even sometimes 10%. (Those who have no Utrecht Atlas available may find a reproduction of one of its pages in just this wavelength region in the paper by McKellar (1942).) The radial component of the earth's orbital motion and its rotation cause a Doppler shift of the whole spectrum which may have an appreciable further effect; it was not taken into account and thus provides another source of error. With cometary spectra a considerable change in radial velocity is required to affect the spectrum seriously; thus, this error should be small. Each branch of each band was followed a little beyond $K'' = 40$; for those lines with a measured spin splitting both intensities were read and then averaged.

The tracings in the Utrecht Atlas were supposed to be adjusted so that the continuum was at the 100% level. It has since been discovered by Chalonge and co-workers that in the near ultraviolet the continuum is well above 100% in places, primarily because of the wings of Balmer lines (Canavaggia and Chalonge 1946; Canavaggia, Chalonge, Egger-Moreau, and Oziol-Pelley 1950; brief summary by Minnaert 1953). The best estimate of the corrections by Michard (1950) are as follows: the continuum taken as having a color temperature of 7150° K is at 114% from 3926 to 3892 Å, and at 124% from 3893 to 3793 Å. The discontinuity occurs in the middle of the 0-0 band and must be taken into account, especially in the case of radiative equilibrium.

Calculations for radiative equilibrium were made by means of (4) except that the weights used were 0.70 and 0.30 because of a numerical error. It was not thought worth while to repeat the calculation, especially since the result

neglects all the other bands of the system and a slightly too large weight for the 0-1 band would help to compensate for this. B'' was taken as 1.922 cm^{-1} (Childs 1932; Herzberg 1950). Separate calculations were made for odd and even levels and the results are shown separately in Fig. 5(b) by means of lines joining the plotted points; the observations are shown by the dots. The two sets could be combined by assuming them to be populated according to the ratio of their statistical weights, but there did not seem to be any advantage to this. Since the ordinate scale is logarithmic, the various sets of points can be moved up and down without change of shape; this procedure was used to fit the corresponding ones together as well as possible. The vertical displacement between the odd and even lines is arbitrary. While there is agreement in some places, the general fit between theory and observation is poor.

Equation (7) was used to calculate the results for thermal equilibrium. The temperature assumed was 2100° K as found in Section 3 from the observations; another calculation using 1700° was also made, but this temperature was obviously too low. The weights used for the two bands were the ones in (4); this result is given in Fig. 5(a) along with the observations. The 2:1 intensity alternation has been removed by doubling the measured intensities of the weak lines; this gives a smoother plot which is easier to interpret. The agreement between calculation and observation is considered to be good and to show that the distribution of rotational levels in the ground state is close to a Boltzmann

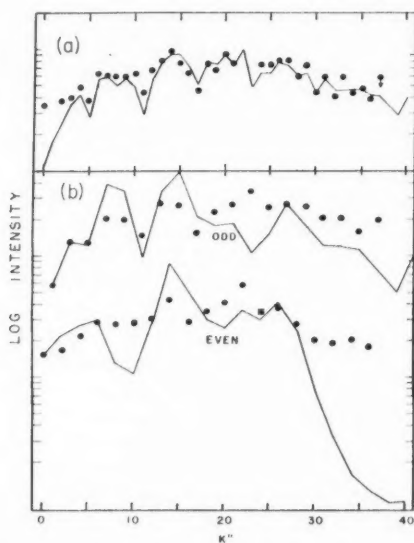


FIG. 5. (a) The synthetic spectrum of the 0-0 band for thermal equilibrium, indicated by lines joining the calculated points. The observations are shown by the dots. Since the ordinate scale is logarithmic, the spectrum can be displaced vertically by any desired amount. The observed intensities of the weak lines have been doubled.

(b) Similar plots for radiative equilibrium. An arbitrary displacement has been used to separate the lines of odd and even K'' .

one. The biggest disagreements are found at the ends of the branch where the lines are faintest and the measurements least certain; in addition, the first few lines ride above an intense series of P lines which must be subtracted. The possible errors in the calculations have already been discussed; the principal ones are the errors in the fractional intensities of the sunlight and the omission of the weaker bands of the system.

TABLE I

Observed intensities of the R lines in the sunlit spectrum, corrected for the presence of the P branch. Also included are the calculated Fraunhofer correction factors \bar{u} defined in the text after equation (7)

K''	Observed intensity	K'	\bar{u}	K''	Observed intensity	K'	\bar{u}
0	299	1	182	23	215	24	105
1	74	2	177	24	631	25	143
2	315	3	178	25	318	26	144
3	169	4	199	26	676	27	188
4	406	5	195	27	331	28	180
5	163	6	108	28	496	29	153
6	537	7	206	29	318	30	174
7	256	8	193	30	368	31	125
8	513	9	147	31	257	32	165
9	255	10	158	32	343	33	149
10	533	11	126	33	254	34	149
11	184	12	71	34	366	35	165
12	574	13	132	35	200	36	178
13	345	14	181	36	323	37	169
14	826	15	201	37	241	38	180
15	328	16	193	38		39	161
16	533	17	157	39	<100	40	147
17	195	18	110	40	234	41	215
18	646	19	167	41	200	42	153
19	288	20	156	42	190	43	143
20	764	21	188	43	100		
21	326	22	158	44	186		
22	(1-1 head)	23	214				

Once it has been established that excitation is from a ground state with a Boltzmann energy distribution, a more accurate temperature for this distribution can be found by modifying the standard plot of $\log(I/K')$ vs. $K'(K'+1)$ to take account of the Fraunhofer lines. As is well known (Herzberg 1950), this follows from an equation similar to (5); $(2K+1)$ is replaced by K' to take into account a slight dependence of transition probability on K' . Since the excitation is now described by (7), the ordinate must be changed to $\log(I/K'\bar{u})$, where \bar{u} is the average residual intensity defined after (7). Such a plot is shown in Fig. 6 along with what is thought to be the most probable straight line; it gives a temperature of 2150° K. Adding the correction of 50° for the slope of the solar continuum, we find 2200° K as the final result; it could probably be in error by $\pm 200^\circ$. The line was drawn to favor the points from $K'' = 15$ to 21 and 30 to 35; the points at the ends are uncertain for the reasons already discussed, and the ones between 22 and 29 appear to be raised by the presence of the 1-1 band. The values of \bar{u} used are given in Table I along with the measured line intensities.

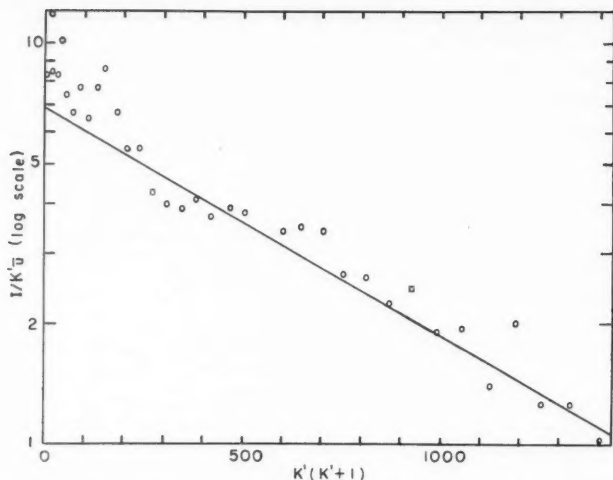


FIG. 6. Plot of $\log I/K'u$ against $K'(K'+1)$ for finding the rotational temperature. Intensities of the weak lines have been doubled.

For later discussion it will be convenient to have an estimate of the rotational "temperature" corresponding to the distribution for radiative equilibrium. The representation by a temperature is not very good, but a plot of the synthetic spectrum according to (7) gave 1200°K for the strongest part of the band. This is much lower than the solar "continuum" temperature because of a number of strong, wide absorption lines in the region of the *R* branch of the 0-0 band; prominent among these is *H*-zeta.

7. DISCUSSION

In this section we wish to discuss the relation between the rotational and vibrational temperatures of the ions and the kinetic temperature of the atmosphere. Since the term "temperature" is used in a somewhat specialized sense, it will be best to review this first. It may be assumed that the N_2 molecules are in thermal equilibrium, so that it is strictly correct to speak of rotational and vibrational temperatures which are equal to the kinetic temperature T . But we observe N_2^+ ions, not neutral molecules, and the observed rotational and vibrational "temperatures" may differ from T ; in such a case it is not strictly correct to use the term temperature, but it is convenient to use it as a parameter which specifies the distribution among the states. We will use the term RT to represent the rotational "temperature", and VT the vibrational "temperature", of the ground state of the ion $X^2\Sigma$. The observed intensities actually give the distributions in the excited state $B^2\Sigma$, but since the excitation mechanism is known the ground-state distributions can be deduced. This was done for the rotation in Section 6, and for the vibration in Section 4.

The processes that control RT and VT will now be considered. First we have the original ionization process



X will usually be an electron even if the primary particles are fast protons because of the large number of fast secondaries (Omholt 1959; Bates, McDowell, and Omholt 1957). The measured cross sections indicate that most of the N_2^+ ions are produced in their ground electronic state (Omholt 1959). Franck-Condon factors for this process are given by Bates (1949a) and from these it is easy to calculate VT as a function of T . (In general there is no guarantee that the vibrational distribution resulting from excitation or ionization can be represented by a temperature, but in this case a good representation is possible.) The result is shown in Fig. 7. For low T , VT is about 1400° K,

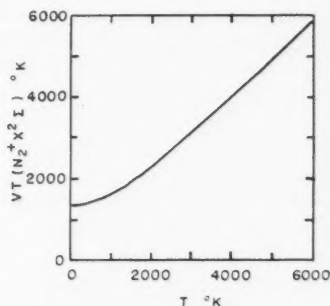


FIG. 7. Effective vibrational temperature of the ground state of the N_2^+ ion resulting from electron impact on N_2 at temperature T .

reflecting the transition probabilities from the lowest vibrational level; for the range 2000° to 3000° which interests us most, VT is about 250° higher than T . To a first approximation, RT is unchanged by ionization because of the restriction of the selection rule and the small change in internuclear distance. However, the actual effect is easily found since the RT's are in the same ratio as the B values; thus, $RT = 0.96 T$.

If X in (8) is a slow proton the most probable reaction is charge exchange in which the electron after the collision is bound to X . Experiments bearing on this process have been made most recently by Fan (1956), Carleton (1957), and Roesler, Fan, and Chamberlain (1958). They seem to show that there is no change in RT at any energy, but a considerable increase in VT around a bombarding energy of 20 kev. The effect on VT when the initial temperature is high is not known, but there would probably still be some increase. Thus one would expect to find VT greater than RT if charge-exchange excitation were affecting VT appreciably, but RT would still be nearly the same as T . No significant difference was observed for either the sunlit or the non-sunlit aurora.

The life of an ion is ended by recombination

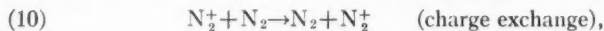


which has a large coefficient; the value $4.0 \times 10^{-7} \text{ cm}^3/\text{sec}$ has been measured (Faire and Champion 1959). A lower value may be more appropriate for our purpose, since the molecules in the laboratory afterglow may well be vibrationally excited; we adopt $4 \times 10^{-8} \text{ cm}^3/\text{sec}$ which may be as much as an order of magnitude too small. In the presence of aurora, the electron density is probably rather higher than normal; we assume $n(e) = 5 \times 10^5/\text{cm}^3$.

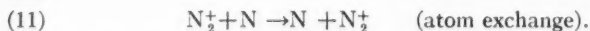
The mean life of an ion is thus only about 50 seconds; a smaller electron density will give a longer life, but it is unlikely to exceed 200 seconds and may be as short as 5 seconds. In this short time RT and VT are not able to depart very far from their original values; thus, the cycle (8) and (9) is effective in keeping the ions close to thermal equilibrium and is by far the most effective process at high altitudes.

As the ion scatters solar radiation, its vibrational and rotational distributions are altered; the final result for the latter is discussed in Sections 5 and 6, and for the former by Bates (1949a). As we have seen, the rotational distribution, for the case of radiative equilibrium, can be represented roughly by $RT = 1200^\circ \text{ K}$. The corresponding VT may be found by comparing Bates' Tables 12 and 13, and is about 4200° K . Both temperatures differ from the sun's color temperature because of the effect of Fraunhofer lines. The speed at which radiative equilibrium is approached depends first of all on the rate of scattering, which was calculated by Bates (1949b). Lytle and Hunten (1960) have revised the result to agree with more recent measurements, and find 0.11 quantum/ion sec for the whole negative system; thus, the mean time between scatterings is 9 seconds. If the estimate of the lifetime of an ion given above is correct, it can scatter only 5.5 quanta, on the average, before recombining; even the longest reasonable life of 200 seconds permits only 22 quanta. Because of the selection rule ($\Delta K = \pm 1$) and the large number of rotational levels, the rotational distribution can be affected only slightly in this time; neither restriction operates on the VT which may rise rather rapidly towards 4200° K . The observed value will be a time average and will lie between ($T + 250^\circ$) and 4200° , probably closer to the lower limit. If T is near 2200° as it appears to be, RT may be slightly less than its original value $0.96 T$.

Let us now consider the effect of collisions with other gas molecules. It is known (Massey and Burhop 1952) that rotational energy is easily transferred; but vibrational energy transfer is essentially impossible on the time scale we are concerned with. For N_2^+ in the atmosphere there are, however, two special processes which effectively do cause rapid transfer of both types of energy:



and



Charge exchange creates a new ion for which RT and VT are both equal to T . The effect of atom exchange is not so obvious, but it seems likely to cause

equipartition among rotational, vibrational, and translational degrees of freedom; thus, if VT was large before the reaction, RT will be increased after it. This seems to be the only mechanism by which RT can become greater than T .

The coefficients for (10) and (11) may be of the order of gas-kinetic, or 3×10^{-10} cm³/sec. If they are to compete effectively with (8) and (9) the mean time between reactions must be less than about 30 seconds, so that the density of N_2 or N must be at least 10^8 particles/cm³. The corresponding height may be estimated with the aid of Nicolet's model of the thermosphere (1959): 250 to 300 km for N_2 and not far above 100 km for N . Rotational energy can be transferred to atomic oxygen, presumably again with about a gas-kinetic cross section requiring as before a density of 10^8 atoms/cm² which is found in the 400- to 500-km region.

Finally, the possibility of direct excitation by electrons should be considered. Excitation accompanies only a few per cent of ionizations, but each ionization is followed by the scattering of five or six photons. Similarly, excitation of the ion by electron impact during its short life is improbable. Photon excitation is always much more important than electron excitation, with the latter serving only to produce the ions so that they may scatter light.

We conclude that above about 300 km the only important reactions are (8) and (9); RT is approximately equal to T and VT somewhat higher. Below 300 km, exchange reactions become more important and RT and VT should not differ appreciably from T . Our aurora was probably well above 300 km, perhaps at 400 or 500 km, and gave RT as 2200° K and VT about 2050° K. Thus it appears that T was not far below 2200° K. Whether this should be taken as the temperature of the normal atmosphere is another question, since considerable energy was being deposited by reactions such as (8) and by the action of solar radiation in raising VT. That VT is found to be less than RT instead of greater is not significant, since neither is accurate to better than $\pm 200^\circ$.

Some accepted conclusions about sunlit and "low-latitude" aurora must be reviewed in the light of our results. In Section 4 it was shown that VT cannot be found from the spectrum without first making a substantial correction for the overlapping of bands which occurs when RT is high. Since this high RT was not suspected previously, many erroneous VT have been derived.

The measurements of Störmer (1939, 1955) on blue sunlit rays were used by Bates (1949a) to deduce that VT corresponded with the value expected from radiative equilibrium as closely as would be expected. Study of Störmer's microphotometer tracing shows that the appearance of the 4278-Å group is very similar to that of Fig. 4, though of much lower dispersion. Störmer gives the intensity ratio (0-1):(1-2) as 100:59; this is to be compared with our uncorrected result of 100:39. It is highly probable that the true intensity ratio is close to our 100:26 and the VT close to 2050° K. The lower resolution of Störmer's spectrum would be expected to raise the uncorrected intensity of the 1-2 band as observed.

A curious type of auroral spectrum has sometimes been observed from low latitudes (Rayleigh 1922; Barbier 1947), and more recently from the latitude

of Moscow (Mironov, Prokudina, and Shefov 1959). Its characteristics are the very high apparent VT shown by the N_2^+ first negative bands and the almost complete absence of the N_2 second positive bands. Both these facts strongly suggest that the aurora is sunlit, an idea which is by no means new (Seaton 1956; notice in particular his statement that Barbier's aurora may have been sunlit despite earlier statements to the contrary). Sunlit aurora should be observable for long distances because of its great height, and its spectrum observed from far away is less likely to be contaminated by light from ordinary aurora than when it is observed from below (Chamberlain and Meinel 1954). On the other hand, it seems likely to be more contaminated by other high-altitude emissions than the spectrum of Störmer which was produced by guiding on visible rays. All the "low-latitude" spectra mentioned were produced by long unguided exposures, though in some cases the sunlit phase must have been rather short. It would seem that "high-altitude" rather than "low-latitude" is the important characteristic of this aurora, although the latter name has the advantage of established usage.

All the "low-latitude" spectra appear to show an even greater development of the negative system than Störmer's; this is particularly evident in the 4709 Å sequence in which the 1-3 band is brighter than the 0-2 and the 2-4 as bright. Unfortunately, our spectrum did not cover this region, but one of the plates by Mironov, Prokudina, and Shefov (1959, Fig. 5) covers it very well. Fortunately, the resolution of this spectrum is just good enough to show some lines of certain multiplets of OII whose other lines must be blended with the heads of the two anomalously intense bands. A rough allowance for these lines brings the relative intensities into reasonable agreement with Störmer's. The 0-1 and 1-2 bands are the most likely to be free of blends; they appear very similar to ours. Their Fig. 6 shows a 0-0 band whose appearance strongly suggests a high RT.

It is suggested that some of the exposure to the atomic lines may have accumulated during the night before the visible aurora appeared, and that the latter then provided the sunlit N_2^+ bands. A rough calculation of the shadow-height during the visible aurora, using the times and pointing data given, shows that it varied between 410 and 330 km. This is consistent with the hypothesis that the display was sunlit.

8. CONCLUSIONS

The spectra taken of the sunlit auroral rays occurring on September 3, 4, and 5, 1958, have been described. Even by inspection it was clear that the rotational and vibrational "temperatures" of the first negative N_2^+ bands were unusually high. A preliminary value of the former was 2100° K; the latter was found to be about 2050° K by comparison with calculations of Bates. Detailed calculations of the rotational structure resulting from fluorescent excitation by sunlight were made on either of two assumptions: first, that the rotational distribution was determined by the fluorescence process itself ("radiative equilibrium"); and second, that the ground state of the N_2^+ ion had a rotational distribution of the Boltzmann type ("thermal equilibrium"). The second case

gave better agreement with the observed spectrum. It was then possible to derive an improved rotational temperature by a method which took account of the solar Fraunhofer lines, and the result was $2200 \pm 200^\circ \text{K}$.

It thus appears that both the rotational and vibrational degrees of freedom of the ion were near thermal equilibrium with the atmosphere. A discussion of the possible mechanisms of thermal relaxation showed that the most important at high altitudes seems to be the short lifetime of the ion against recombination, after which it is replaced by a new ion. The new ion has a rotational temperature slightly less than the kinetic, and a vibrational "temperature" slightly higher. As photons are scattered the vibrational "temperature" rises rather quickly but the rotation is affected only very slowly. After scattering only a few photons (as few as five or six on reasonable assumptions) the ion recombines. The kinetic temperature in the auroral rays cannot have been much below 2200°K , but the rays may possibly have been hotter than the normal atmosphere.

This work reverses the accepted conclusion that the vibration of the ions is in radiative equilibrium in sunlit auroral rays. Earlier spectra did not have high enough dispersion to show the large rotational temperature which causes neighboring bands to overlap. It appears that "low-latitude" aurora requires the same correction, and also others for blending with atomic lines. With these corrections this type of aurora gives results very similar to those found in this paper.

ACKNOWLEDGMENTS

This investigation was greatly aided by a number of people whose contributions are appreciated. H. J. Koenig operated the spectrographs and the unique spectra resulted from his excellent guiding. The synthetic spectrum of Fig. 4 was calculated by A. E. Johanson. Contributions to the interpretation were made by J. F. Noxon, J. W. Chamberlain, and especially D. R. Bates.

REFERENCES

- BARBIER, D. 1947. *Ann. géophys.* **3**, 227.
BATES, D. R. 1949a. *Proc. Roy. Soc. (London)*, **A**, **196**, 217.
——— 1949b. *Proc. Roy. Soc. (London)*, **A**, **196**, 562.
BATES, D. R., McDOWELL, M. R. C., and ÖMHOLT, A. 1957. *J. Atmospheric and Terrest. Phys.* **10**, 51.
CANAVAGGIA, R. and CHALONGE, D. 1946. *Ann. astrophys.* **9**, 143.
CANAVAGGIA, R., CHALONGE, D., EGGER-MOREAU, M., and OZIOL-PELLEY, H. 1950. *Ann. astrophys.* **13**, 355.
CARLETON, N. P. 1957. *Phys. Rev.* **107**, 110.
CHAMBERLAIN, J. W. and MEINEL, A. B. 1954. *The earth as a planet*, edited by G. P. Kuiper (University of Chicago Press).
CHILDS, W. H. J. 1932. *Proc. Roy. Soc. (London)*, **A**, **137**, 641.
CLARK, K. C. and BELON, A. E. 1959. *J. Atmospheric and Terrest. Phys.* **16**, 205.
FAIRE, A. C. and CHAMPION, K. S. 1959. *Phys. Rev.* **113**, 1.
FAN, C. Y. 1956. *Phys. Rev.* **103**, 1740.
HERZBERG, G. 1950. *Spectra of diatomic molecules* (D. Van Nostrand Co., Inc., New York).
HUNTEN, D. M. 1955. *J. Atmospheric and Terrest. Phys.* **7**, 141.
HUNTEN, D. M., KOENIG, H. J., and VALLANCE JONES, A. 1959. *Nature*, **183**, 453.
LYTLE, E. A. and HUNTEN, D. M. 1960. *Can. J. Phys.* **38**, 477.
MASSEY, H. S. W. and BURHOP, E. H. S. 1952. *Electronic and ionic impact phenomena* (Oxford University Press).

- McKELLAR, A. 1942. *Revs. Modern Phys.* **14**, 179.
- MICHARD, R. 1950. *Bull. Astron. Inst. Netherlands*, **11**, 227.
- MINNAERT, M. 1953. *The sun*, edited by G. P. Kuiper (University of Chicago Press).
- MINNAERT, M., MULDER, G. F. W., and HOUTGAST, J. 1940. *Photometric atlas of the solar spectrum* (Sonneborg Observatory, Utrecht).
- MIRONOV, A. V., PROKUDINA, V. S., and SHEFOV, N. N. 1959. *Spectro- and electro-photometrical and radar researches of aurora and airglow* (Academy of Sciences, Moscow).
- NICOLET, M. 1959. *Ann. géophys.* **15**, 1.
- OMHOLT, A. 1959. *Geofys. Publikasjoner* (Oslo), **20**, No. 11.
- PETRIE, W. and SMALL, R. G. 1952. *Astrophys. J.* **116**, 433.
- RAYLEIGH, Lord. 1922. *Proc. Roy. Soc. A*, **101**, 114.
- ROESLER, F. L., FAN, C. Y., and CHAMBERLAIN, J. W. 1958. *J. Atmospheric and Terrestrial Phys.* **12**, 200.
- SEATON, M. J. 1956. *The airglow and the aurorae*, edited by E. B. Armstrong and A. Dalgarno (Pergamon Press, London).
- SHEPHERD, G. G. 1954. *Scientific Report No. AR-16*, U.S.A.F. Contract AF 19(122)-152. (University of Saskatchewan).
- STÖRMER, C. 1939. *Terrestrial Magnetism and Atmospheric Elec.* **44**, 7.
- 1955. *The polar aurora* (Oxford University Press).
- SWINGS, P. 1941. *Lick Observatory Bull.* **19**, 131.
- 1943. *Monthly Notices Roy. Astron. Soc.* **103**, 86.
- 1949. *The atmospheres of the earth and planets*, edited by G. P. Kuiper (University of Chicago Press).
- WALLACE, L. V. and NICHOLLS, R. W. 1955. *J. Atmospheric and Terrestrial Phys.* **7**, 101.

DAWN ENHANCEMENT OF AURORAL N_2^+ EMISSION¹

E. A. LYTLE AND D. M. HUNTEN

ABSTRACT

The 0-0 band at 3914 Å was observed once per minute with a scanning spectrometer as sunlight illuminated the upper atmosphere on the morning of September 5, 1958. It is reasonable to assume that the density of N_2^+ ions was maintained constant during this time, and that the observed rise of intensity was due to resonance scattering of sunlight. The ions were found to be distributed between 180 and 320 km with peak at 250; density here was 12×10^4 ions/cm³. There was some evidence for another layer at 120 km. Rotational temperatures measured while the main layer was fully illuminated agreed well and gave an average of $1060 \pm 100^\circ$ K.

1. INTRODUCTION

Measurement of rotational temperature of N_2^+ bands in aurora has been carried out for many years. This experience has shown that it is difficult to find measurable aurora much above 100 km, most temperatures being below 400° K. Sunlit auroral rays are much higher (Störmer 1955) and are bright enough to give a good spectrum of the 0-0 band (3914 Å) in a short time. An accompanying paper (Vallance Jones and Hunten 1960) gives details of the measurements of high sunlit rays on September 4, 5, and 6, 1958, with a high-dispersion spectrograph. During the same display it was possible to observe continuously the dawn enhancement on September 5 with a scanning spectrometer at 1 spectrum/minute. There is reason to suppose that the N_2^+ density was maintained constant during the half-hour required for this enhancement; its vertical distribution can then be found by well-established methods used for twilight analysis. The ions were found to occupy a layer about 100 km thick; measurement of intensity gave a peak density of 12×10^4 ions/cm³ at 250 km. The measured rotational temperature of 1060° K presumably applies to this mean height and should be essentially equal to the kinetic temperature of the atmosphere.

2. OBSERVATIONS

The spectrometer was used with a resolution of 2 Å, normal for rotational-temperature work with this instrument (Shepherd and Hunten 1955). It is usual to make scans lasting 10 seconds on aurora, but on this occasion the amplifier for the high-speed recorder was not working and it was necessary to use a slower one at 1 scan/minute. Fortunately, the aurora was unusually quiet, especially during the dawn enhancement; thus, the slow scans were no disadvantage and in fact gave improved sensitivity. The typical spectrum shown in Fig. 1 illustrates the low dispersion and appreciable noise level; but

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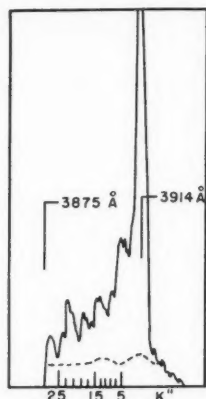


FIG. 1. Sample spectrum taken at a shadow height of 150 km. The estimated solar background is shown also.

the results are consistent from scan to scan and appear reliable. The region covered was from 3875 Å to somewhat past the head at 3914 Å; while this normally includes the whole of the 0-0 band, it did not do so this time because of the high temperature which was not recognized until later; lines with K'' greater than 26 were missed. It is now obvious that the filling in of the zero gap by the returning P branch indicates the high temperature immediately; normal aurora shows the gap clearly at the resolution used (Shepherd and Hunten 1955).

Towards morning the aurora was observed to be rather faint but with constant and fairly uniform intensity all over the sky. Scattered clouds were present but had no observable effect on the intensity, presumably because they were well illuminated by auroral light. The sky was fairly clear in the north; the spectrometer was left pointing in this direction at a zenith angle of 55°. Since the sun rises almost exactly in the east at this time of year, the shadow height for observations to the north is the same as in the zenith. The intensity as a function of shadow height is shown in Fig. 2, with an indication of time

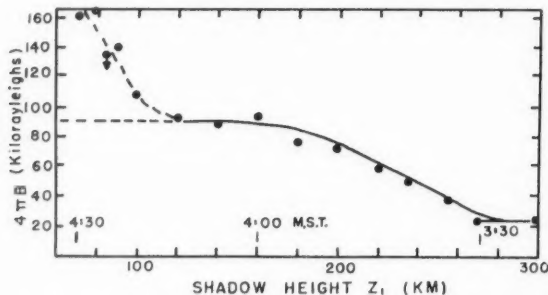


FIG. 2. Band intensity as a function of geometrical shadow height z_1 . Mountain Standard Time (105th meridian) is also shown. Each point is an average of about five individual spectra.

as well. The intensity remained at 24 kilorayleighs (kR) for at least 20 minutes, until the shadow reached the 280-km level; it then steadily rose to 86 kR between 170 and 120 km. The further rise starting at 120 km seems to be real, but the measurements in this region are unreliable because a large continuous background had to be subtracted; it was equal to the band intensity at 90 km. The assumption that the enhancement was entirely due to resonance is seen to be reasonable, but it cannot be proved. Proof might have been obtained by measuring some other emission which does not come from a resonance transition, but this was not feasible.

Rotational temperatures were measured for the region 200 to 140 km when the intensity was nearly constant. The unresolved profiles were corrected for convergence of the lines as described by Shepherd and Hunten (1955). The plots of $\log(I/K')$ vs. $K'(K'+1)$ gave the expected straight line for K'' between 15 and 25; below 15 the returning P branch raises the intensity and this was observed. The effect is illustrated by Hunten, Koenig, and Vallance Jones (1959) for a higher temperature obtained during the same display. The spectra were averaged in four groups of 5 giving temperatures of 1100, 1125, 1000, and 1025° K; the average of these is 1060° K. As the shadow fell still more, the temperature seemed to rise still higher, but this measurement is even more unreliable than the intensity one at low shadow-heights, because even a small error in estimating the continuous background could give a large error in the temperature. The measurements given for the greater shadow-heights are not appreciably affected by this difficulty.

3. N_2^+ DENSITY AND DISTRIBUTION

To find the vertical distribution of N_2^+ ions we must differentiate the curve of Fig. 2; this can only be done roughly but at least the heights at which the derivative goes to zero are reasonably well defined. The symmetrical curve chosen is shown in Fig. 3. As for any twilight investigation, we also need to calculate the transmission of the lower atmosphere as a function of height above and below the geometrical shadow, since this gives the form of the shadow imposed on the incident sunlight. The calculation was done essentially as described by Hunten (1954) using an extinction coefficient of 0.040 per atmosphere (Allen 1955); this includes a small contribution from ozone which was lumped in with the rest since it is so small. Dust in the lowest atmosphere was represented by a coefficient of 0.042 per atmosphere falling off with a scale height of 1.0 km. Numerical differencing of the final table of T gave dT/dz_1 which we call $\dot{T}(z_1+x)$; z_1 is the geometrical shadow-height used in Section 2. \dot{T} is plotted in Fig. 3; the center of mass is 29 km above the geometrical shadow and the second moment is 62 km². It has recently been shown (Hunten 1959) that the brightness derivative plotted against $(z_1+29$ km) as in Fig. 3 may be regarded as the ion distribution broadened by a "slit function" \dot{T} . From the relative breadths of these two curves it may be seen that the broadening is negligible considering the uncertainties in the observations, and this is confirmed by trying the sharpening procedure used for twilight sodium observations. Figure 3 thus gives the ion distribution directly. If the lower layer is really present, its height would be about $90+29 \div 120$ km, a common height for aurora.

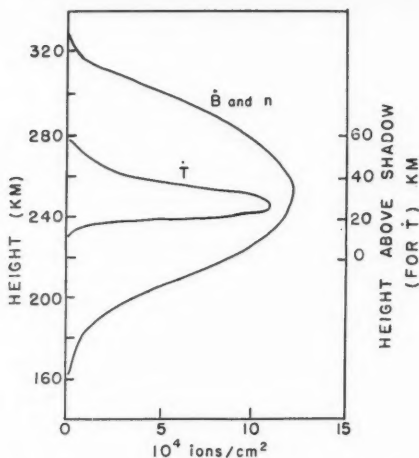


FIG. 3. \dot{B} , estimated derivative of Fig. 2 plotted against $(z_1 + 29)$ km. \dot{T} , derivative of the transmission function plotted against the height above the geometrical shadow; this height is shown at the right. n , N_2^+ ion density (units of 10^4 ions/cm³).

To find the total amount of N_2^+ we use the observation that resonance produced a brightness of $86 - 24 = 62$ kR at a zenith angle of 55° . Presumably the same layer seen in the zenith would be fainter by the van Rhijn factor 0.616 calculated for a height of 250 km; this gives a zenith brightness of 38 kR. According to the Appendix, N_2^+ illuminated by sunlight scatters 0.068 quantum/ion sec; thus we have $(38/0.068) \times 10^9 = 5.6 \times 10^{11}$ ions/cm² (column). The half-thickness of the layer shown in Fig. 3 is about 90 km; thus, the average density is about 6×10^4 ions/cm³ and the peak 12×10^4 . This gives the ion-density scale in Fig. 3.

4. DISCUSSION

It should be repeated that most of this analysis rests on the assumption that the ion density remained constant during the 30 or 40 minutes taken by the shadow to sweep over the 200- to 300-km region. While this is plausible, there is no way of being sure without other measurements which were not made. The height distribution found is similar to that of high auroral rays, though we do not suggest that the observations were of ray structures, rather, of a sort of afterglow remaining from a night of unusually strong and high aurora. The high sunlit rays observed in the evenings of September 4 and 5 were presumably a somewhat different phenomenon; this is confirmed by their higher temperature of about 2300° K which suggests a higher altitude of around 500 km.

Our rotational temperature of $1060 \pm 100^\circ$ K does not depend on the above assumption and seems reliable. This temperature is a reasonable one for a height of 250 km, and probably agrees with the kinetic temperature there as

suggested by the analysis of Vallance Jones and Hunten (1960). The N_2^+ ions apparently occupied a layer between 180 and 320 km with peak at 250. Their abundance was 5.6×10^{11} ions/cm² (column) and the peak density 12×10^4 ions/cm³. These numbers were deduced from a brightness $4\pi B = 62$ kR for the dawn enhancement observed at a zenith angle of 55° .

If another opportunity comes to observe high sunlit aurora with a scanning spectrometer, the scan should if possible be extended to 3840 Å to include the lines of higher rotation. Since this type of aurora is not very bright but is rather quiet, 1-minute scans can be used and perhaps wider slits, 4 or 5 Å instead of 2 Å, preferred for normal aurora. The better resolution is required only for the region near the origin which is useless in high-temperature aurora because of the presence of high lines of the *P* branch.

If at all possible, a twilight series of the kind discussed here should be accompanied by measurements of a bright line or band which shows no resonance enhancement. This would allow a check on our assumption that the N_2^+ density remained constant during the twilight. A bright band of the N_2 second positive system would probably be best.

REFERENCES

- ALLEN, C. W. 1955. *Astrophysical quantities* (Athlone Press, London), p. 116.
 BATES, D. R. 1949. *Proc. Roy. Soc. (London)*, A, **196**, 562.
 DALBY, F. W. and BENNETT, R. G. 1959. *Symposium on molecular structure and spectroscopy*, Ohio State University, Columbus.
 HUNTEN, D. M. 1954. *J. Atmospheric and Terrest. Phys.* **5**, 44.
 ——— 1959. *J. Atmospheric and Terrest. Phys.* In press.
 HUNTEN, D. M., KOENIG, H. J., and VALLANCE JONES, A. 1959. *Nature*, **183**, 453.
 SHEPHERD, G. G. and HUNTEN, D. M. 1955. *J. Atmospheric and Terrest. Phys.* **6**, 328.
 SHULL, H. 1950. *Astrophys. J.* **112**, 352.
 ——— 1951. *Astrophys. J.* **114**, 546.
 STÖRMER, C. 1955. *The polar aurora* (Oxford University Press).
 VALLANCE JONES, A. and HUNTEN, D. M. 1960. *Can. J. Phys.* **38**, 458.

APPENDIX

SCATTERING POWER FOR THE 0-0 BAND OF AN N_2^+ ION

The fundamental calculation of this quantity was made by Bates (1949). The ions were taken as having a rotational temperature of 273° K, and the exciting intensities at each line were found from the Utrecht Atlas of the solar spectrum. For the case in which collisions could be neglected, he found 0.13 quantum scattered per ion per second for the whole band system, and 60% of this in the 3914-Å band. An oscillator strength $f = 0.04$ was calculated and used. A rather larger value was calculated later by Shull (1950, 1951), but a recent measurement by Dalby and Bennett (1959) agrees better with Bates' result: $f = 0.0348 \pm 0.002$. Combining this with Bates' figure given above, we find a scattering power for the 0-0 band of 0.068 quantum/ion sec. This is not strictly correct for our much higher rotational temperature, but should not be greatly in error.

ROTATIONAL SPECTRUM OF $K^{39}F$ BY THE MOLECULAR BEAM ELECTRIC RESONANCE METHOD¹

G. W. GREEN² AND H. LEW

ABSTRACT

Transitions between the $J = 0$ and $J = 1$ rotational states of $K^{39}F$ have been measured by means of the molecular beam electric resonance method. The following rotational constants have been determined (all frequencies in Mc/sec):

$$\begin{array}{ll} Y_{01} = B_e & 8392.312 \pm 0.006 \\ -Y_{11} = \alpha_e & 69.991 \pm 0.010 \\ Y_{21} = \gamma_e & 0.204 \pm 0.005 \\ B_e & 8392.482 \pm 0.070 \end{array}$$

The quadrupole interaction constants eqQ as measured in the $J = 1$ state are found to be

$$\begin{array}{ll} v = 0 & -7.932 \pm 0.003 \text{ Mc/sec}, \\ v = 1 & -7.835 \pm 0.010 \text{ Mc/sec}. \end{array}$$

The equilibrium internuclear distance obtained directly from B_e is

$$r_e = (2.17144 \pm 0.00005) \times 10^{-8} \text{ cm.}$$

The electric dipole moment in the $v = 0$ state is

$$\mu_E = (8.60 \pm 0.09) \times 10^{-18} \text{ e.s.u.}$$

INTRODUCTION

When the rotational spectrum of RbF was obtained in this laboratory (Lew *et al.* 1958), the remaining alkali halides for which the rotational constants were unknown were LiF , NaF , KF , and $LiCl$; these had all proved unsuitable for microwave absorption methods (Honig *et al.* 1954). Since KF was expected to have the lowest rotational frequencies among these molecules, it was the next one chosen for investigation. From the equilibrium internuclear distances calculated by Honig *et al.*, the $J = 1 \leftarrow J = 0$ frequency was estimated to be $17,400 \pm 175$ Mc/sec.

Potassium fluoride has been studied twice previously by beam methods: each time by observations of the radio-frequency transitions between Stark sublevels of particular rotational states. Grabner and Hughes (1950) obtained values for the quadrupole interaction energy eqQ_K^* in the vibrational states $v = 0, 1, 2, 3, 4$, an estimate of the dipole moment and of the moment of inertia in the zeroth vibrational state, and also the vibrational constant ω_e from intensity measurements in several vibrational states. Schlier (1957)

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*In this work, the quadrupole interaction constant will be denoted by eqQ rather than eqQ/h , for instance, regardless of the units in which the quantity is expressed. This is consistent with the practice of using B_e for the equilibrium rotational constant no matter whether it is given in ergs, cm^{-1} , or Mc/sec.

obtained more accurate values for the quadrupole interaction using a multipole version of the electric resonance apparatus to refocus $J = 1, 2$, and 3 states and also obtained values for the spin-rotation ($I.J$) interaction constants C , for both the F and K nuclei.

In the present experiment, through the observation of $J = 1 \leftarrow J = 0$ transitions, we have obtained the molecular rotational constants B_e and α_e and the electric dipole moment μ_E and also obtained quadrupole interaction constants in agreement with those of Grabner and Hughes and Schlier.

THEORY

The rotational spectrum obtained in this experiment is analyzed by means of Dunham's expressions for the energy levels of a vibrating rotator. The frequencies of the rotational transitions in the first four vibrational states in the absence of hyperfine structure (h.f.s.) are given in terms of the Dunham coefficients by Dunham (1932) and are restated by Lew *et al.* (1958). In order to use these expressions, the h.f.s. of the $J = 1$ state must be taken into account. The major contribution to h.f.s. in KF is due to the quadrupole moment of the K^{39} nucleus which has a spin of $3/2$; fluorine, with spin $1/2$, has no quadrupole moment. The h.f.s. pattern due to the K^{39} quadrupole was determined with the aid of the table of Casimir's function given by Townes and Schawlow (1955, Appendix I, p. 517) and with the aid of the experimental results of Schlier (1957) or of Grabner and Hughes (1950). First-order separations were found to be 1.5 to 2 Mc/sec; second-order energies were in no case greater than 0.1 kc/sec and were quite negligible (Townes and Schawlow 1955, Appendix II, p. 517). Further h.f.s. arises from the spin-rotation ($I.J$) interactions for both nuclei. Schlier's values for these interaction constants are

$$C_F = +10.55 \pm 0.07 \text{ kc/sec,}$$

$$C_K = 0.380 \pm 0.097 \text{ kc/sec.}$$

Neglecting the potassium $I.J$ interaction, we find for the h.f.s. of the $J = 1$ state the pattern shown in Fig. 1. The magnitude of the $I_F.J$ splitting has been calculated from eq. 8 of Nierenberg, Rabi, and Slotnick (1948). This shows that the maximum splitting occurs in line Y and is approximately 12.7 kc/sec. It was expected that such a splitting would be observed and although a splitting did appear in some traces it was not reproducible consistently and could not be attributed unambiguously to the $I.J$ interaction.

The electric dipole moment may be determined by observing the change in transition frequencies on application of a static voltage to the C field. The most suitable line for this measurement is line Z (Fig. 1). From eq. 10-31 of Townes and Schawlow (1955, p. 261), the $F_1 = 1/2$ level of $J = 1$ is neither split nor shifted by a weak field. Thus the only change in the transition frequency arises from a shift of the $J = 0$ level. This is given by (eq. 10-19, Townes and Schawlow)

$$(1) \quad \Delta W_{J=0} = -\mu_E^2 E^2 / 6B_e.$$

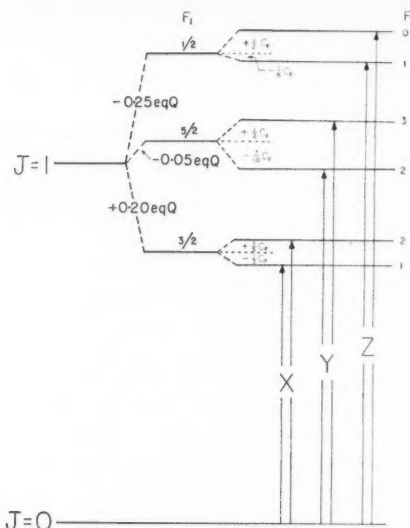


FIG. 1. Energy levels of the $J = 0$ and $J = 1$ rotational states of $K^{39}F$. $F_1 = J + I_K$, $F = F_1 + I_F$.

Using Grabner and Hughes' estimate of μ_E it is seen that C fields of up to 30 volts/cm produce shifts of less than 0.5 Mc/sec and satisfy the "weak field" condition that

$$\mu_E^2 E^2 / B_e \ll eqQ.$$

APPARATUS

The apparatus has been described by Lew *et al.* (1958). The previously used FP-54 d-c. amplifier was replaced by an Applied Physics Corporation vibrating reed electrometer (model 31) using a 5×10^{10} -ohm input resistor and taking the electrometer output via an integrating circuit to a Leeds and Northrup 20-millivolt pen recorder. This system gave an over-all sensitivity of 1 inch per 5×10^{-14} ampere although it was usually employed at 1/3 or 1/10 of this sensitivity. The surface ionization detector was a specially treated tungsten wire* in which the potassium contamination had been largely removed. The background ion current from the special wire, though still appreciable, was much less than that from commercial tungsten wires. Under our experimental conditions the best signal-to-noise ratio was obtained with an oxidized tungsten wire at a temperature of about 1150° K. The absolute detection efficiency at this temperature is not known. After oxidation the efficiency was found to decrease slowly over the course of several hours. Hence a capillary supply of air to the filament was provided to permit periodic re-oxidation without loss of vacuum.

*This wire was kindly supplied by Mr. E. P. Kilroy, General Electric Company, Cleveland, Ohio.

An attempt was made to improve the signal-to-noise ratio by chopping the beam at 15 cycles/sec and using a tuned a-c. amplifier, integrator, and recording system. This had very poor sensitivity except at high-filament temperatures where filament noise was prohibitive. The poor efficiency was attributed to the filament time constant being greater than the chopping period and the inverse dependence of this time constant on the filament temperature.

ELECTRONIC EQUIPMENT

Two modifications were made to the arrangement described by Lew *et al.* (1958). The first was the replacement of the Varian X-12 klystron by a Sperry 2K39 for measurements on the $v = 0$ transitions. This change was necessary because the Varian klystron had a large bandwidth at the higher frequency end of its range. Since the Sperry klystron had a frequency range of 7,500 to 10,300 Mc/sec, it was necessary to feed the output into a crystal rectifier and use the second harmonic for the inducement of transitions. The second modification was the conversion of the frequency multiplier chain to give an output at 540 Mc/sec instead of 270 Mc/sec. The sequence of multiplications is then 1-5-10-30-60-180-540 Mc/sec. The 31st harmonic and associated markers could then be used for klystron stabilization and frequency measurement rather than the much weaker 62nd harmonic of 270 Mc/sec.

The klystron control remained the same as that used by Lew *et al.* but since a recording system was used, the tuning condenser of the frequency modulation receiver was driven by a synchronous motor rather than being set manually as previously.

EXPERIMENT

The production of a beam of KF molecules presented no difficulties: an oven temperature of 875° to 900°C as measured by an iron-constantan thermocouple produced an ion current at the detector of 2 to 3×10^{-9} ampere. Commercial $\text{KF} \cdot 2\text{H}_2\text{O}$ was used; a load of several grams filled the oven up to the bottom of the slit and was sufficient for a month's work.

The refocussed beam was found to be 2 or 3 times greater than the predicted fraction (1 part in 10^4) of the main beam; part of this is accounted for by states other than $J = 0$ being refocussed. Under the best conditions the refocussed beam was several times the magnitude of the residual beam, the residual beam being defined as that arriving at the detector with the stop-wire in position and the B field on but the A field off, the refocussed beam being defined as the increase in detected beam on switching on the A field.

The time constant of the detection system introduced a delay between a transition and its recording. This resulted in a difference between apparent transition frequencies measured in opposite directions of scan. As the rate of scan was sometimes as high as 1 kc/sec per sec, this difference could amount to 10 kc/sec or more. Consequently each quoted transition frequency is the result of averaging several scans in each direction and then taking the mean of the two averages.

Errors attached to quoted frequencies cover the range of measured values and are such as to give self-consistency for quantities such as eqQ calculated from several frequency differences.

RESULTS AND DISCUSSION

A. Observed Lines, Quadrupole Interactions

Rotational transitions belonging to the three vibrational states $v = 0, 1, 2$ were observed. These are listed in Table I. Typical recordings of several of these are shown in Fig. 2. These are all for the line $(J = 1, F_1 = 3/2) \leftarrow (J = 0)$

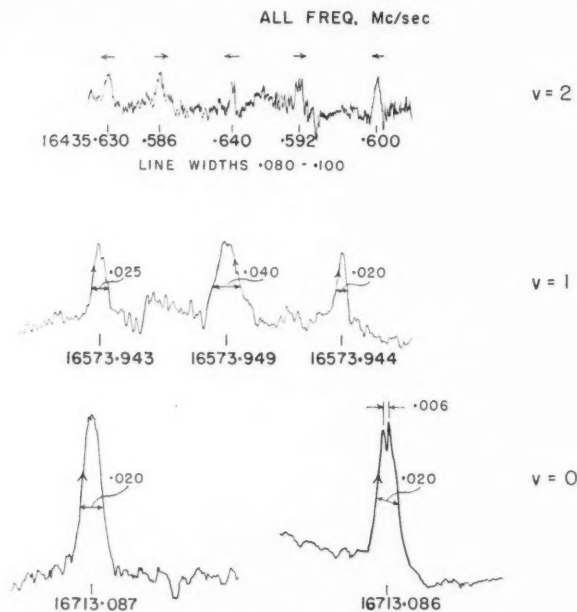


FIG. 2. Some typical transitions in K_2F : the line $(J = 1, F_1 = 3/2) \leftarrow (J = 0)$ for $v = 0, 1, 2$. For a given vibrational state the successive peaks shown are repeated observations of the same line, the arrows indicating the direction of increasing frequency scan. The frequencies shown are not corrected for a departure of about 5 parts in 10^7 of the 1 Mc/sec standard from its nominal value. The correction is made in the values tabulated in Table I.

for the three observed vibrational states. It can be seen how the signal-to-noise ratio decreases rapidly in the measurements of the higher vibrational states. The line width increases at the same time, probably because greater microwave power was required for the weaker lines. The .006-Mc/sec splitting shown in one of the $v = 0$ lines was initially ascribed to the $I_F.J$ interaction but attempts to reproduce it consistently were not successful. A similar but larger splitting was observed in line Y (Fig. 1). Since the splittings were not reproducible, they would not appear to be due to $I_F.J$ interaction. Their origin is not known. No correction is made for the effect of a finite C field caused by

contact potential as it is shown below that this amounts at most to 0.4 kc/sec and is therefore within the accuracy of our measurements.

TABLE I
Observed frequencies $J = 1 \leftarrow 0$ (Mc/sec)

Line	F_1 of $J = 1$ level	$v = 0$	$v = 1$	$v = 2$
Z	1/2	16,716.653 \pm 0.0015	16,577.462 \pm 0.005	
Y	5/2	16,715.067 \pm 0.001	16,575.897 \pm 0.005	16,437.542 \pm 0.010
X	3/2	16,713.083 \pm 0.001	16,573.936 \pm 0.005	16,435.599 \pm 0.010

The quadrupole interaction constants as measured in the $J = 1$ rotational state are given in Table II. The values obtained by Schlier and by Grabner and Hughes are shown for comparison. It is seen that good agreement exists in the cases of $v = 0$ and $v = 1$, where our results are obtained from all three

TABLE II
Values of eqQ (Mc/sec) as measured in the state $J = 1$

v	Schlier	Grabner and Hughes	This work
0	-7.9347 \pm 0.0011	-7.938 \pm 0.040	-7.932 \pm 0.003
1	-7.8391 \pm 0.0012	-7.828 \pm 0.040	-7.835 \pm 0.010
2	-7.7435 \pm 0.0013	-7.744 \pm 0.040	-7.772 \pm 0.055
3		-7.658 \pm 0.040	

lines, X, Y, and Z (Fig. 1). In the case of $v = 2$ where our result is obtained from the lines X and Y only, agreement is not so good but our result still overlaps that of Schlier within the large uncertainty quoted.

B. Rotational Constants

The positions of the rotational levels are determined in the absence of h.f.s. by the use of Fig. 1. In the case of $v = 2$ where there is considerable uncertainty in our value of eqQ , Schlier's value was used in conjunction with our measurement of the stronger line Y. The difference between the value so obtained and that obtained using our value of eqQ is only 1 kc/sec. The rotational transition frequencies unperturbed by h.f.s. are then as shown in Table III.

TABLE III
Calculated rotational transition frequencies in the absence of h.f.s.
(Mc/sec) ($J = 1 \leftarrow 0$)

$v = 0$	16,714.670 \pm 0.002
$v = 1$	16,575.504 \pm 0.005
$v = 2$	16,437.155 \pm 0.010

The rotational constants calculated from these frequencies are shown in Table IV. For these calculations, use was made of the values of $Y_{10} \approx \omega_e = 400 \text{ cm}^{-1}$ and $Y_{20} \approx \omega_e x_e = 1.45 \text{ cm}^{-1}$ obtained by Barrow and Caunt

(1953) from ultraviolet absorption spectra. By assuming probable errors of 5% and 20% in these values of ω_e and $\omega_e x_e$, respectively, we obtain $B_e = Y_{01} + (0.170 \pm 0.068)$ Mc/sec. Thus the quoted error in B_e arises almost entirely from the errors in the vibrational constants.

TABLE IV
Rotational constants of K^{39}F (Mc/sec)

$Y_{01} \approx B_e$	8392.312 ± 0.006
$-Y_{11} \approx \alpha_e$	69.991 ± 0.010
$Y_{21} \approx \gamma_e$	0.204 ± 0.004
B_e	8392.482 ± 0.070

C. Internuclear Distance

By using the relation $B_e = \hbar^2/2I$ we may obtain the value of the moment of inertia

$$I = (99.9809 \pm 0.0036) \times 10^{-40} \text{ g cm}^2.$$

In order to obtain the equilibrium internuclear distance r_e , it is usual to assume that the reduced mass μ , obtained from the atomic weights of the atoms concerned, may be substituted in the equation $I = \mu r_e^2$. The value we obtain in this way is

$$r_e = (2.17144 \pm 0.00005) \times 10^{-8} \text{ cm}$$

where the error arises almost entirely from those in Planck's constant and the atomic mass unit (Cohen *et al.* 1955). Although this calculation neglects several electronic effects in the molecule the above value of r_e is probably the best one obtainable in the absence of an exact knowledge of the molecular wave functions. The electronic effects neglected are:

(i) The Ionic Nature of the Molecule

The reduced mass of an ionic molecule cannot be obtained from the neutral atomic masses in the usual way because of the displacement of the valency electron. If we calculate the extreme case of this effect, where the valency electron is considered to be at the fluorine nucleus, we find that the change in r_e only amounts to -0.00002×10^{-8} cm which is negligible when compared with the experimental error in r_e .

(ii) Electron Slip during Molecular Rotation

This may occur both in valency electrons and in electrons bound to specific nuclei. Valency electrons having a spherical distribution about the molecular center of mass will be undisturbed by molecular rotation. Closed shells of electrons having a spherical distribution about a nucleus will follow the nucleus during molecular rotation but their orientation will remain fixed in space. However, in an ionic molecule, polarization will distort such spherical shells and the slip will be reduced.

We have calculated the contribution to the moment of inertia of the slip of bound electrons by use of eq. 8-34 of Townes and Schawlow. By assuming that no polarization exists and that all electrons are distributed in spherical

shells about their respective nuclei we are able to find the maximum contribution of this type of slip. The equilibrium internuclear distance then becomes

$$r_e^* = 2.17113 \times 10^{-8} \text{ cm}$$

which differs from the previous value by 1 part in 10^4 . Because of the approximations used in the above treatment, no great reliance can be attached to this value and the previous value of r_e obtained directly from B_e will be used in the remaining discussion.

It is of interest to note that our observed value of r_e is approximately 2% higher than that calculated by Honig *et al.* on the basis of an empirical relation which they had found to be accurate to 1% in all other cases of alkali halides. This unexpectedly large discrepancy led to a considerable waste of time in the search for KF transitions, as it did for Barrett and Mandel (1954) with the high-temperature microwave spectrometer.

Pauling (1956) has published a treatment of interatomic distances in alkali halide gas molecules which is simpler than that of Honig *et al.* By using the Born expression for the repulsive potential between two ions and neglecting any polarization effects, Pauling has derived a simple formula for r_e in terms of ionic radii r^+ and r^- which had been previously obtained for crystals (Pauling 1948):

$$r_e = (r^+ + r^-)(0.291)^{1/(n-1)}$$

where n is the Born exponent of repulsive potential and $(0.291)^{1/(n-1)}$ is the factor representing the ratio of distances in the vapor and crystalline phases (see Honig *et al.* 1954, p. 638). He then assumes that n , which varies from molecule to molecule, may be written as $n = n^+ + n^-$, where n^+ is to be associated with the positive ion and n^- with the negative. Apparently by using 8 out of the 15 experimental values of r_e which were known at the time of his writing, he was able to assign values to the n^+ 's for all the alkalis and to the n^- 's for all the halides. With these he was then able to calculate values of r_e for the other seven molecules which turned out to be in better agreement with experiment than Honig's; this is not surprising considering the number of standards used. Pauling's calculated values are shown in Table V along with the experimentally observed values. For comparison, values calculated by Honig *et al.* and by Krasnov (1959) are also included. As his standards, Pauling had presumably chosen the five bromides and CsF, KCl, and KI, for we were able to reproduce his calculated values most closely using these standards. The n^+ and n^- we used are not identical with Pauling's but it is believed that the latter had rounded his numbers off to the first place after the decimal. The values we used are $n^+ = 4.004, 4.690, 4.656, 4.520, 4.189$ for $\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{and Cs}^+$ respectively and $n^- = 2.073, 3.949, 4.500, 5.299$ for $\text{F}^-, \text{Cl}^-, \text{Br}^-, \text{and I}^-$ respectively. It should be pointed out that the n^+ and n^- are not uniquely determined by the experimental data; other sets are permissible.

From Table V it can be seen that Pauling's calculated internuclear distances for the fluorides are not in very good agreement with the experimental values.

TABLE V

Comparison between experimental and calculated equilibrium internuclear distances in alkali halide gas molecules (in units of 10^{-8} cm)

	Experimental	Honig <i>et al.</i>	Pauling	Present authors using Pauling's method	Krasnov
LiF	1.51 ± 0.08	1.527	1.518	1.527	1.584
NaF	—	1.840	1.833	1.856	1.917
KF	2.171	2.129	2.130	2.154	2.166
RbF	2.265	2.246	2.239	2.265(s)	2.259
CsF	2.345	2.346	2.345(s)	2.370	2.345(s)
LiCl	—	2.022	2.027		2.037
NaCl	2.361	2.356	2.353		2.361(s)
KCl	2.667	2.667(s)	2.667(s)		2.667(s)
RbCl	2.787	2.793	2.790		2.787(s)
CsCl	2.906	2.911	2.916		2.906(s)
LiBr	2.170	2.166	2.170(s)		2.170(s)
NaBr	2.502	2.500	2.502(s)		2.503
KBr	2.821	2.815	2.821(s)		2.821(s)
RbBr	2.945	2.944	2.945(s)		2.948
CsBr	3.072	3.065	3.072(s)		3.075
LiI	2.392	2.392	2.392		2.385
NaI	2.712	2.727	2.722		2.719
KI	3.048	3.051	3.048(s)		3.048(s)
RbI	3.177	3.182	3.174		3.180
CsI	3.315	3.307	3.306		3.315

NOTE: The quantities with (s) after them are those used as standards.

If instead of CsF we use RbF as the standard for the fluorides we get the values given in the fifth column in Table V. The average agreement with experiment for the fluorides is improved while for all the other alkali halides the agreement is unchanged. More recently, Krasnov (1959) has adapted the empirical relation of Honig *et al.* and obtained the best agreement so far between calculated and experimental values of the interatomic distances in alkali halide gas molecules.

He uses the equation

$$r_e = r_1 + r_2 - \frac{4(\alpha_1 + \alpha_2)}{(n-1)(r_1 + r_2)}$$

where α_1 and α_2 are the polarizabilities of the two ions, n is the Born exponent, and r_1 and r_2 are no longer the crystal ionic radii but are the ionic radii of free ions. A set of values of r_1 and r_2 are obtained by using certain experimental values of r_e as standards in much the same way as Pauling obtained his sets of n^+ and n^- . Once the r_1 's and r_2 's are known then the r_e 's for the remaining molecules may be calculated. These values are shown in Table V. The improved agreement, particularly for the fluorides is immediately noticeable, the values predicted for RbF and KF agreeing to within 0.006×10^{-8} cm. It is therefore believed that Krasnov's results would be the most reliable for predicting transition frequencies of the remaining alkali halides (LiF, NaF, and LiCl).

D. Dipole Moment

As was mentioned earlier, the line Z was chosen for the measurement of the electric dipole moment in the $v = 0$ state. Static voltages of up to 12 volts

were applied to the C field in which the gap was 0.69065 cm. The shift Δf in the frequency of the line was measured with the static voltage first in one direction and then in the other. For $V_c = +12$ volts, $\Delta f = 0.122 \pm 0.002$ Mc/sec, for $V_c = -12$ volts, $\Delta f = 0.103 \pm 0.002$ Mc/sec. The difference between the two frequency shifts is caused by the contact potential of the C field. For this particular measurement the contact potential was 0.51 ± 0.09 volt. The electric dipole moment in the $v = 0$ state is then found by eq. 1 to be

$$\mu_E = (8.60 \pm 0.09) \times 10^{-18} \text{ e.s.u.}$$

This value may be compared with that of $(7.33 \pm 0.24) \times 10^{-18}$ e.s.u. obtained by Grabner and Hughes and of 8.07×10^{-18} e.s.u. calculated from Rittner's (1951) expression.

The contact potential of the C field is a variable quantity dependent upon the immediate history of the vacuum. Its highest measured value was 0.7 volt. This will affect the energy levels at nominally zero field. The $J = 0$ level shows the strongest dependence on the field and it is seen that for a field of 1.013 volts/cm corresponding to a contact potential of 0.7 volt, the shift in this level is 0.00038 Mc/sec. This is considerably smaller than frequency measurement errors in this experiment.

Although the values of the individual quantities μ_E and r_e (or B_e) as given by Grabner and Hughes have been shown to be in considerable error, it is of interest to note that the value they get for the composite quantity $\hbar^2 \mu_E^2 / 2B_e$ is in excellent agreement with ours. They quote $\mu_E = (7.33 \pm 0.24) 10^{-18}$ e.s.u., $\hbar^2 / 2B_e = (138.4 \pm 6.9) 10^{-10}$ g.-cm². Hence, ignoring the stated uncertainties for reasons given below the Grabner and Hughes' value is

$$\hbar^2 \mu_E^2 / 2B_e = 7436 \times 10^{-76} \text{ g.cm}^2 \text{ e.s.u.}^2$$

while we find (this work)

$$\hbar^2 \mu_E^2 / 2B_e = 7394 \times 10^{-76} \text{ g.cm}^2 \text{ e.s.u.}^2.$$

This agreement is not surprising. The frequency of the ΔM_J transition they observed is expressible in the form (Hughes 1949)

$$\Delta f(1,0 \rightarrow 1, \pm 1) = \alpha E^2 - \beta E^4 + \gamma E^6$$

where E is the strength of the electric field in which the transition takes place:

$$\alpha = \frac{0.15}{h} \left(\frac{\mu_E^2}{B_e} \right), \quad \beta = \frac{0.01076}{h} \left(\frac{\mu_E^4}{B_e^3} \right), \quad \gamma = \frac{0.00125}{h} \left(\frac{\mu_E^6}{B_e^5} \right).$$

Thus it is seen that if the departure of the observed frequency from a quadratic dependence on E is small, i.e. if $\alpha \gg \beta$, then α may be determined with much greater accuracy than β . Since α immediately yields a value for μ_E^2/B_e while a knowledge of β is required for the extraction of the individual quantities μ_E and B_e , it is seen why the above agreements and discrepancies have occurred. For this reason too, the uncertainties quoted by Grabner and Hughes for the individual quantities cannot be carried over to the quantity $\hbar^2 \mu_E^2 / 2B_e$.

If we substitute the accurate value of B_e found in the present work into the quantity $\hbar^2\mu_E^2/2B_e$ as found by Grabner and Hughes, we find

$$\mu_E = 8.63 \times 10^{-18} \text{ e.s.u.}$$

which agrees with our value very well.

The dipole moments of most of the alkali fluorides and of the alkali chlorides are now known. These are shown in Table VI (following Kusch and Hughes (1959), but with some later entries). It should be noted that for the fluorides the dipole moment reaches a peak at RbF as one goes down the column from Li to Cs. The dipole moment of CsF is distinctly smaller than that of RbF or KF. This does not seem to be the case in CsCl as compared with KCl.

TABLE VI
Permanent electric dipole moments of alkali fluorides and chlorides in Debyes
(for vibrational state $v = 0$)

F			Cl	
Li	6.6 ± 0.3	Braunstein and Trischka (1955)	5.9 ± 1.3	Marple and Trischka (1956)
Na	—		8.5 ± 0.2	Tate and Strandburg (1954)
K	8.60 ± 0.09	Present work	10.48 ± 0.05	Lee <i>et al.</i> (1953)
Rb	8.80 ± 0.10	Lew <i>et al.</i> (1958)		
Cs	7.875 ± 0.006	Trischka (1956)	10.42 ± 0.02	Trischka (1956)

E. Relationships between the Rotational and Rotational-Vibrational Constants in the Alkali Halides

(i) B_e and α_e

By assuming that the potential energy of a diatomic molecule may be described by a Morse function, Pekeris (1934) obtained the relationship

$$(2) \quad \alpha_e = \frac{6\sqrt{\omega_e x_e B_e^3}}{\omega_e} - \frac{6B_e^2}{\omega_e}$$

If in this relation we substitute values of ω_e and $\omega_e x_e$ as tabulated in Honig *et al.* (1954) we find for α_e the values indicated by crosses in Fig. 3. For comparison the experimental values are also plotted and are indicated by dots. It is seen that the experimental points fall very nearly on a straight line which satisfies the relation (with the variables in megacycles per second)

$$(3) \quad \alpha_e = 2.15 \times 10^{-4} B_e^{1.4}$$

In the case of the calculated points, however, at least part of the scatter must be ascribed to uncertainties in ω_e and $\omega_e x_e$.

Equation 3 proved of considerable help in finding transitions in neighboring vibrational states once the first transition had been found, since from the simple theory of rotational transitions

$$f_{J+1, v-0} - f_{J, v-0} = 2B_v = 2[B_e - \alpha_e(v + \frac{1}{2})].$$

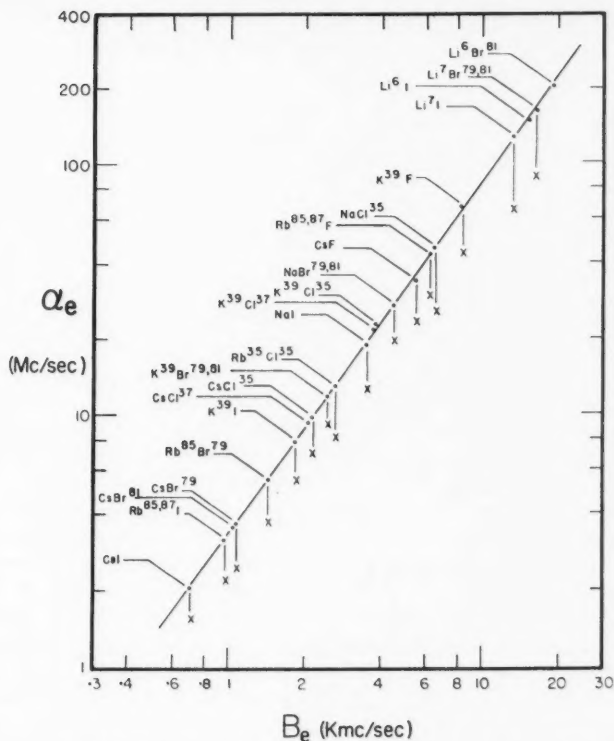


FIG. 3. A plot of α_e vs. B_e for the alkali halides. Except for RbF and KF , values are taken from Honig *et al.* The values of ω_z and $\omega_z \nu_e$ used in the calculated values of α_e are also from Honig *et al.* ● Experiment, X calculated.

(ii) B_e and γ_e

It is seen from Fig. 4 that the graph of $\log \gamma_e$ versus $\log B_e$ is also roughly linear in form but with considerable scatter. Expressing the variables in megacycles per second, the plot may be represented by the relation

$$(4) \quad \gamma_e = 1.16 \times 10^{-8} B_e^{1.88}.$$

From the figure again it can be seen that the CsF point deviates from the mean line by a much larger amount than any of the other points. The possibility of an error is suggested. An examination of the experimental data of Honig *et al.* shows that, with their errors of from 0.2 to 1.0 Mc/sec in the measured transition frequencies, the error in the value of γ_e can be much larger than as stated by the authors. Whether the accurately linear dependence of $\log \alpha_e$ on $\log B_e$ and the similar though less accurate one between $\log \gamma_e$ and $\log B_e$ has any fundamental significance or not is not known.

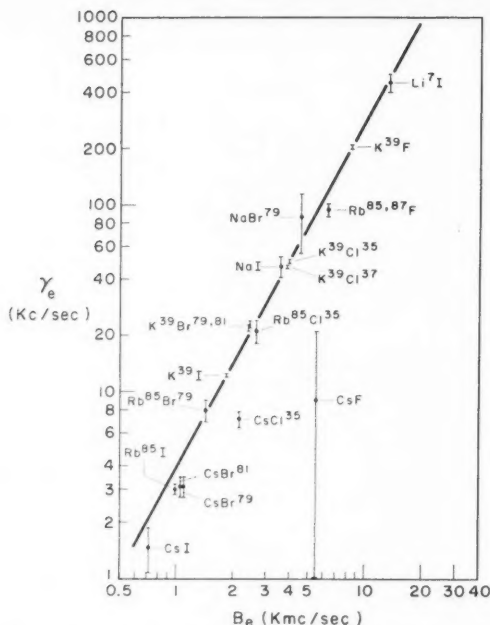


FIG. 4. A plot of γ_e vs. B_e for the alkali halides. Except for RbF and KF, values are taken from Honig *et al.*

REFERENCES

- BARRETT, A. H. and MANDEL, M. 1954. Columbia Radiation Laboratory Quarterly Report, Jan. 30, p. 18.
- BARROW, R. F. and CAUNT, A. D. 1953. Proc. Roy. Soc. (London), A, **219**, 120.
- BRAUNSTEIN, R. and TRISCHKA, J. W. 1955. Phys. Rev. **98**, 1092.
- CARLSON, R. O., LEE, C. A., and FABRICAND, B. P. 1952. Phys. Rev. **85**, 784.
- COHEN, E. R., DRUMMOND, J. M. W., LAYTON, T. W., and ROLLETT, J. S. 1955. Revs. Modern Phys. **27**, 363.
- DATZ, S. and TAYLOR, E. H. 1956. J. Chem. Phys. **25**, 395.
- DUNHAM, J. L. 1932. Phys. Rev. **41**, 721.
- GRABNER, L. and HUGHES, V. 1950. Phys. Rev. **79**, 819.
- HONIG, A., MANDEL, M., STITCH, M. L., and TOWNES, C. H. 1954. Phys. Rev. **96**, 629.
- HUGHES, H. K. 1947. Phys. Rev. **72**, 614.
- 1949. Phys. Rev. **76**, 1675.
- KRASNOV, K. C. 1959. Zhur. Neorg. Khim. **4**, 530.
- KUSCH, P. and HUGHES, V. W. 1959. Handbuch der Physik, Vol. 37 (Springer-Verlag, Berlin), p. 1.
- LEE, C. A., FABRICAND, B. P., CARLSON, R. O., and RABI, I. I. 1953. Phys. Rev. **91**, 1395.
- LEW, H., MORRIS, D., GEIGER, F. E., Jr., and EISINGER, J. T. 1958. Can. J. Phys. **36**, 171.
- MARPLE, D. T. F. and TRISCHKA, J. W. 1956. Phys. Rev. **103**, 597.
- NIEKENBERG, W. A., RABI, I. I., and SLOTNICK, M. 1948. Phys. Rev. **73**, 1430.
- PAULING, L. 1948. Nature of the chemical bond, 2nd ed. (Cornell University Press, Ithaca, N.Y.).
- 1956. Proc. Natl. Acad. Sci. India, A, **XXV**, 1.
- PEKERIS, C. L. 1934. Phys. Rev. **45**, 98.
- RITTNER, E. S. 1951. J. Chem. Phys. **19**, 1030.
- SCHLIER, C. 1957. Z. Physik, **147**, 600.
- TATE, P. A. and STRANDBERG, M. P. 1954. J. Chem. Phys. **22**, 1380.
- TOWNES, C. H. and SCHAWLOW, A. L. 1955. Microwave spectroscopy (McGraw-Hill Book Co., Inc.).
- TRISCHKA, J. W. 1956. J. Chem. Phys. **25**, 784.

SPIN-LATTICE RELAXATION EFFECTS OBSERVED IN THE CONTINUOUS POWER SATURATION OF PARAMAGNETIC LINES¹

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ABSTRACT

The dependence of the conventional saturation parameter on the incident microwave power is considered for Lorentzian-shaped paramagnetic lines and applied to a study of the ($-\frac{1}{2} \rightarrow +\frac{1}{2}$) transitions of Cr^{+++} in $\text{K}_3\text{Co}(\text{CN})_6$ and Gd^{+++} in $\text{La}(\text{C}_2\text{H}_3\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ at 9 kMc/sec and 4.2° K. It is shown that the experimental observations may be explained on the basis of a spin-lattice transition probability which depends on spin-photon interactions. Values of the effective spin-lattice relaxation times are compared with pulse technique determinations and estimates of the corresponding phonon relaxation times are also given.

1. INTRODUCTION

With the advent of the solid-state maser suggested by Bloembergen (1956) and successfully demonstrated by Scovil, Feher, and Seidel (1957) and others using magnetically dilute paramagnetic crystals, the need for a clearer understanding of the processes involved in the transfer of energy from the paramagnetic ion to the lattice is required for the development of other suitable maser materials. In particular, the processes involved which determine the spin-lattice relaxation times are important. The experiments of Bloembergen, Purcell, and Pound (1948) show that the relaxation of nuclear magnetic states can be adequately explained by the Bloch equations (1946) with the aid of spin-spin and spin-lattice relaxation times. The success of these experiments, in which the onset of non-linearity or saturation between the incident power and the absorbed power is measured, led to the application of similar techniques to electron paramagnetic resonance (Eschenfelder and Weidner 1953; Feher and Scovil 1957; Giordmaine, Alsop, Nash, and Townes 1958).

An alternative approach to the problem has also been successfully employed (Davis, Strandberg, and Kyhl 1958), in which the paramagnetic sample is subjected to a high-power pulse of radiation, sufficient to saturate the sample, and the regrowth of the absorption is followed by means of a small monitoring signal. The exponential rise of the peak of the absorption line allows a value of the spin-lattice relaxation time T_1 to be determined. Davis *et al.* have pointed out that the value of T_1 obtained by their experiment decreases with increase in monitoring power and that their low power values are much larger than continuous power saturation experiments performed under similar conditions. In an earlier paper, Strandberg (1958) indicated that T_1 may depend upon the degree of saturation present if phonons play a significant part in the relaxation process.

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The purpose of the present paper is to report the results of measurements performed on some paramagnetic resonance lines over a range of continuous power levels and to show how the results may be interpreted on the basis of a spin-lattice transition probability which changes with the incident power on the paramagnetic crystal.

II. THEORY

The magnetic properties of a paramagnetic substance can be described in terms of the complex magnetic susceptibility, where the imaginary part, χ'' , is responsible for the absorption of the microwave energy in the medium. χ'' at a frequency ν is given by

$$(1) \quad \chi''(\nu) = \frac{1}{2} \pi \chi_0 \nu_0 Z g(\nu)$$

where χ_0 is the static susceptibility, $g(\nu)$ the shape factor of the line concerned, Z the saturation term, and ν_0 the frequency at peak absorption. Studies of the paramagnetic spectra of

Cr^{+++} in $\text{K}_2\text{Co}(\text{CN})_6$ and on Gd^{+++} in $\text{La}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$

(Swarup 1959) have shown that for small paramagnetic ion concentrations the line shape is Lorentzian. The shape factor may thus be written as

$$(2) \quad g(\nu) = \frac{2T_2}{1 + 4\pi^2(\nu_0 - \nu)^2 T_2^2}$$

where T_2 is the spin-spin relaxation time and is related to the width $\Delta\nu$ of the unsaturated line at half-maximum absorption by

$$(3) \quad T_2 = (\pi\Delta\nu)^{-1}.$$

The saturation term Z is defined by

$$(4) \quad Z = \frac{N_1 - N_2}{N_{10} - N_{20}}$$

where N_1 and N_2 refer to the ion populations of the lower and upper energy states respectively and N_{10} and N_{20} are the equilibrium values in the absence of microwave radiation.

In the nuclear magnetic resonance experiments, the assumption is made (Bloembergen, Purcell, and Pound 1948) that the lattice may at all times be considered in thermal equilibrium with the bath surrounding the sample. Under these conditions, the peak value of the differential of χ'' is given by

$$(5) \quad \left(\frac{d\chi''}{d\nu} \right)_{\text{max}} \propto [1 + \frac{1}{2} \gamma^2 H_1^2 T_1 T_2]^{-3/2}$$

where H_1 is the magnetic component of the linearly polarized radio-frequency field and γ is the gyromagnetic ratio. Equation 5, or some similar expression, is normally employed for the determination of T_1 by determining $(d\chi''/d\nu)_{\text{max}}$ at very low microwave power and when it has decreased by some fraction of its low power value.

While the above assumption is applicable for nuclear magnetic resonance, it is not necessarily valid in electron paramagnetic resonance. For this reason, the saturation term Z should be derived in terms which do not invoke the concept of spin and lattice temperatures as an initial assumption.

The rate of change in the population difference under the influence of microwave power is given by

$$(6) \quad \frac{d(N_1 - N_2)}{dt} = 2N_2W_{21} - 2N_1W_{12} - 2Y(N_1 - N_2)$$

where W_{21} is the transition probability from the upper ionic state to the lattice and W_{12} the transition probability for the reverse process. Y is the transition probability for the stimulated emission and absorption of microwave radiation. The spontaneous transition probability can be neglected in that it is several orders of magnitude less than Y in this region of the spectrum. Under steady-state conditions, the rate of change of population is zero, thus enabling Z to be determined. By standard radiation theory, the value for Y for the $(-\frac{1}{2} \rightarrow +\frac{1}{2})$ transition is given by

$$(7) \quad Y = \frac{1}{4}\gamma^2 H_1^2 g(\nu).$$

Substituting for $Zg(\nu)$ in equation (1) and differentiating w.r.t. ν we obtain

$$(8) \quad \frac{d\chi''}{d\nu} = \frac{1}{2}\pi\nu_0\chi_0 \frac{N_2}{N_{20}} \frac{(W_{21}/W_{12}) - 1}{(W_{21}^0/W_{12}^0) - 1} \frac{16\pi^2 T_2^3 (\nu_0 - \nu)}{[1 + 4\pi^2 (\nu_0 - \nu)^2 T_2^2 + (\frac{1}{2}\gamma^2 H_1^2 T_2^2 / W_{12})]^2}$$

where W_{21}^0 and W_{12}^0 are the thermal equilibrium values of the spin-lattice transition probabilities when Y is zero. By differentiation of equation 8, the peak value of $(d\chi''/d\nu)$ may be obtained as

$$(9) \quad \left(\frac{d\chi''}{d\nu}\right)_{\max} = \frac{1}{2}\pi\nu_0\chi_0 \frac{N_2}{N_{20}} \frac{(W_{21}/W_{12}) - 1}{(W_{21}^0/W_{12}^0) - 1} \frac{3\pi T_2^2}{[1 + (\frac{1}{2}\gamma^2 H_1^2 T_2^2 / W_{12})]^{3/2}}.$$

An examination of equation 9 shows that at least in the early stages of saturation, any significant change in $(d\chi''/d\nu)_{\max}$ must come from within the square bracket and any suspected change of the spin-lattice relaxation time T_1 with saturating power will be indicated by a change in W_{12} itself since T_1 may be written as W_{12}^{-1} .

Van Vleck (1940) considered the spin of the paramagnetic ion to be coupled to the lattice through the mixing of second- and higher-order perturbations of the spin-orbit and orbit-lattice coupling. Such mixing gives rise to spin-lattice matrix elements which depend on the parameters of the spin and electronic state of the ion, and in addition, upon the phonon excitation expressed in terms of a phonon quantum number n . Under these conditions, W_{12} can be written in the form

$$(10) \quad W_{12} = \rho(\nu)A\langle n \rangle$$

where A is the spin transition probability per unit of phonon excitation, $\langle n \rangle$ is the mean phonon quantum number for phonons having a characteristic frequency ν , and $\rho(\nu)$ is the density of phonon modes.

The microwave frequency of 9 kMc/sec used in the experiments is well away from the upper limit for phonon frequencies imposed by the interatomic distances in the lattice and consequently $\rho(\nu)$ can be represented by the Debye approximation as

$$(11) \quad \rho(\nu) = \left[\frac{1}{v_l} + \frac{2}{v_t} \right] 4\pi\nu^2$$

where v_l and v_t are the longitudinal and transverse phonon velocities respectively. In the absence of microwave radiation, energy is exchanged between phonons due to crystal imperfections, the coupling via the paramagnetic ion spins, etc., and the n values tend to fluctuate about their respective equilibrium values $\langle n_0 \rangle$. The probability of a phonon mode having an energy E is governed by a Bose-Einstein distribution, and consequently the thermal equilibrium value of $\langle n \rangle$ is given by

$$(12) \quad \langle n_0 \rangle = \left[\exp \frac{h\nu}{kT} - 1 \right]^{-1}.$$

Under the influx of the microwave radiation, energy is transferred from the spins to the lattice and the rate of change of $\langle n \rangle$ can be written (Strandberg 1958)

$$(13) \quad \frac{d\langle n \rangle}{dt} = \frac{Y(N_1 - N_2)}{V\rho(\nu)\Delta\nu} - \frac{\langle n \rangle - \langle n_0 \rangle}{\tau}$$

where $\Delta\nu$ is the excitation width for phonons in direct contact with the spins and is probably of the same order or less than the width of the resonance line itself. In this paper it is assumed that the two widths are equal; consequently the same symbol ($\Delta\nu$) is used for both widths. τ represents an over-all relaxation time for phonons by way of phonon-phonon and phonon-bath interactions.

For the steady state saturation conditions required here, $d\langle n \rangle/dt$ is zero and the departure of $\langle n \rangle$ from its thermal equilibrium value $\langle n_0 \rangle$ is

$$(14) \quad \Delta n = \frac{Y(N_1 - N_2)}{V\rho(\nu)\Delta\nu} \tau$$

and W_{12} becomes

$$(15) \quad W_{12} = A\rho(\nu)\langle n_0 \rangle \left(1 + \frac{\Delta n}{\langle n_0 \rangle} \right).$$

In the initial stages of saturation, a value for Δn may be obtained by assuming the spin populations do not differ appreciably from their thermal equilibrium values, then substituting for Y , W_{12} may be written

$$(16) \quad W_{12} = A\rho(\nu)\langle n_0 \rangle \left[1 + \frac{\frac{1}{2}\gamma^2 T^2 \tau (N_{10} - N_{20}) H_1^2}{V\rho(\nu)\Delta\nu\langle n_0 \rangle} \right].$$

The expected dependence of $(d\chi''/d\nu)_{\max}$ on H_1^2 , at least in the initial stages of saturation may therefore be written as

$$(17) \quad \left(\frac{d\chi''}{d\nu} \right)_{\max} \propto \left[1 + \frac{KH_1^2}{1 + CH_1^2} \right]^{-3/2}$$

where

$$(18) \quad K = \frac{\frac{1}{2}\gamma^2 T_2}{A\rho(\nu)\langle n_0 \rangle} = \frac{1}{2}\gamma^2 T_2 T_1^0$$

and

$$(19) \quad C = \frac{\frac{1}{2}\gamma^2 T_2 \tau (N_{10} - N_{20})}{V\rho(\nu)\Delta\nu\langle n_0 \rangle}.$$

The difference between equations 17 and 5 is that C may not be zero for paramagnetic resonance.

III. EXPERIMENTAL

A conventional X-band paramagnetic resonance spectrometer utilizing a magic-T impedance bridge was employed. Phase-sensitive detection and amplification of the signal allowed the resonance line to be displayed as a derivative on a Rectiriter chart recorder. The cavity operated in the TE_{102} mode situated between the pole pieces of a 6-in. Varian magnet in suitable low-temperature Dewars. The cavity and crystal were immersed in liquid helium at 4.2° K in order to obtain as good a coupling between the crystal and the low-temperature bath as possible. A 1000 c/s modulation on the magnetic field was kept below a peak-to-peak value of 0.5 oersted. The steady magnetic field was swept at the rate of 2 oersteds/minute and was controlled by the driving motor of the recorder. A Pound stabilized X-13 klystron was used for the low-power measurements and a Sperry 2K39 for high-power saturation measurements. The power entering the cavity was monitored by measuring the reflected power (P_r) by a Polytechnic 650-A universal power bridge. The power incident on the cavity (P_i) was variable over the range 1×10^{-6} to 5×10^{-2} watts.

In conjunction with the observations of other workers (Meyer 1955), an initial experiment showed that the width at half-maximum absorption of a powdered sample of the free radical diphenyl picryl hydrazyl did not change with P_i and that the peak value of the derivative, I_p , increased linearly with increase of P_i over the range of power available. The crystals under study were all of 0.1 cc or less in volume and were placed in the cavity along with a small sample of the powdered D.P.P.H. Values of I_p could then be obtained for both the paramagnetic crystal and D.P.P.H. under identical power conditions. Ratios of I_p for the paramagnetic crystal to I_p for D.P.P.H., made over the range of P_i available, enabled the saturation of the paramagnetic crystal to be measured. These ratios, normalized to unity at low power levels are representative of equation 17. Measurements of the width of the paramagnetic line at low power enabled T_2 to be determined. The relation between H_1^2 and P_i was obtained from

$$(20) \quad H_1^2 = \frac{32}{V^2 \nu} \left(\frac{\lambda}{\lambda_0} \right)^2 Q_L P_i (1 - \Gamma)$$

taken from Meyer (1955) for the field in a rectangular cavity. Q_L is the loaded

Q of the cavity of volume V' and Γ is the reflection coefficient. For the experiments reported here, $Q_L \sim 3000$ and $\Gamma = 0.66$ giving $H_1^2 = 1.6 P_1$ where P_1 is measured in watts.

The crystals studied were $K_3CoCr(CN)_6$ and $LaGd(C_2H_5SO_4)_3 \cdot 9H_2O$ and were prepared by mixing known proportions by weight of the diamagnetic salt with its isomorphous paramagnetic salt, dissolving the mixture in distilled water, and growing the combined crystals by slow evaporation. By this means, crystals were obtained where the nominal percentage of the diamagnetic ions replaced by paramagnetic ions were 0.1%, 0.5%, and 1% for the Cr^{+++} ion and 1% for the Gd^{+++} ion. A determination of the actual percentage made in the case of the 1% crystals by Atomic Energy of Canada Ltd. by X-ray fluorescence showed that the actual concentrations were somewhat less than the nominal concentrations which are used to designate the crystals.

IV. RESULTS

The normalized peak absorption derivative ratios obtained for different values of the microwave power incident on the cavity are shown in Fig. 1 for

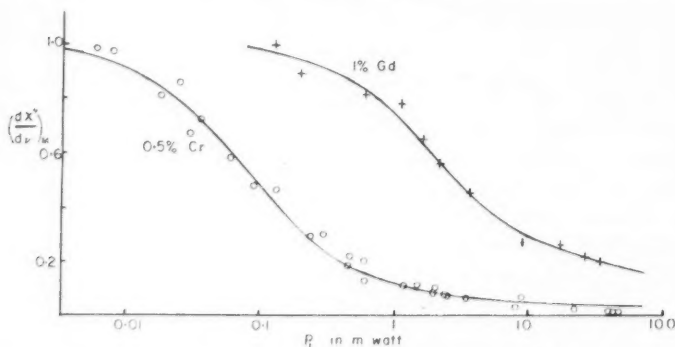


FIG. 1. The saturation of paramagnetic resonance lines at 4.2° K.
 ○ Experimental points for 0.5% Cr^{+++} in $K_3Co(CN)_6$.
 + Experimental points for 1.0% Gd^{+++} in $La(C_2H_5SO_4)_3 \cdot 9H_2O$.
 — Fitted theoretical curves of $\{1 + [KH_1^2/(1 + CH_1^2)]\}^{-3/2}$.

the $(-\frac{1}{2} \rightarrow +\frac{1}{2})$ transitions for the 0.5% Cr^{+++} ion and the 1% Gd^{+++} ion at 4.2° K. The full curves are plots of equation 17 with suitable values of K and C . A constant value for C was indicated from the experimental measurements with a slight departure for the 0.5% Cr^{+++} ion in the region of 10^{-2} to 10^{-1} watt range. This departure can be accounted for by the change in W_{21}/W_{12} and $N_1 - N_2$. The best fits to the experimental data were obtained with $K = 5600 \pm 100$ and $C = 525 \pm 50$ for the 0.5% Cr^{+++} ion and values of $K = 140 \pm 20$ and $C = 47 \pm 5$ for the 1% Gd^{+++} ion.

Attempts were made to extend the measurements on the Cr^{+++} ion to crystals which contained 0.1% and 1% nominal paramagnetic ion concentrations. In the former case, the very low powers needed for saturation and the decrease

in signal-to-noise ratio reduced the accuracy obtainable. In the case of the 1% crystal, an extension of the measurements to higher values of P_1 is required to determine C accurately.

Table I shows the experimental quantities obtained at 4.2° K. The values of T_1^0 are the inverse of the spin-lattice transition probabilities under thermal equilibrium conditions (W_{12}^0). Estimates of τ , the phonon-bath relaxation times, are obtained from the values of C assuming that the populations of the states concerned had not changed appreciably from thermal equilibrium values. Estimates of these populations were made with the aid of the actual concentrations available.

TABLE I
Experimental results at 4.2° K

Crystal*	ΔH , oersteds	T_2 , sec	K	C	T_1^0 , sec	τ , sec	A /sec
Cr 0.1%	6	2×10^{-8}	$\sim 12,500$	$\sim 2,000$	$\sim 5 \times 10^{-3}$	10^{-6}	$\sim 2 \times 10^{-4}$
Cr 0.5%	9	1.3×10^{-8}	5,600	525	2.2×10^{-3}	10^{-7}	4.5×10^{-4}
Cr 1.0% (.13)	14	0.8×10^{-8}	44	1-10	3.5×10^{-3}	10^{-8} - 10^{-9}	3×10^{-2}
Gd 1% (.4)	20.8	0.6×10^{-8}	140	47	1.6×10^{-4}	10^{-7}	6×10^{-3}

*Actual concentrations shown in parentheses.

The change in effective T_1 with saturation is shown more clearly over a limited power range in Fig. 2. For C equal to zero, and consequently a constant

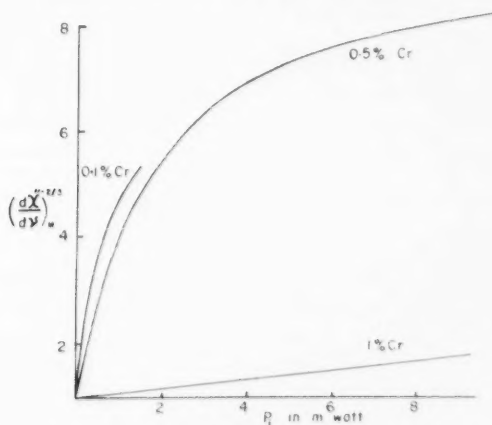


Fig. 2. Saturation curves of 0.1%, 0.5%, and 1.0% Cr^{+++} in $\text{K}_3\text{Co}(\text{CN})_6$ at 4.2° K.

value of T_1 , a straight line would be obtained. While this may be justified for the 1% Cr^{+++} ion at 4.2° K, it is by no means the case for the 0.1% and the 1% Cr^{+++} ion curves.

The absolute values of the relaxation times depend upon a large number of variables; however, they are probably correct to within an order of magnitude.

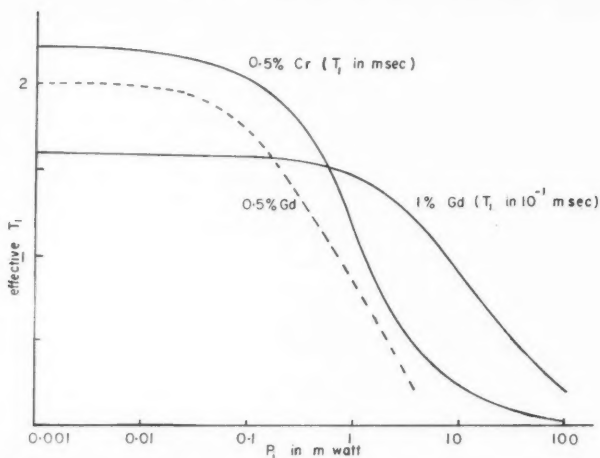


FIG. 3. Plots of effective T_1 with microwave power.

Full curves, 0.5% Cr^{+++} in $\text{K}_2\text{Co}(\text{CN})_6$ and 1% Gd^{+++} in $\text{La}(\text{C}_2\text{H}_3\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ from continuous power saturation experiments.

Dotted curve: values obtained by Davis *et al.* (1958) for 0.5% Gd^{+++} in $\text{La}(\text{C}_2\text{H}_3\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.

The change in T_1 observed by Davis *et al.* for a crystal containing a nominal concentration of 0.5% Gd^{+++} in $\text{La}(\text{C}_2\text{H}_3\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, using their pulse technique and varying the monitoring power, is shown in Fig. 3 with the power level arbitrarily placed on the logarithmic scale (since the absolute power levels were not available). Also shown are the variations in the effective T_1 values for the 0.5% Cr^{+++} and the 1% Gd^{+++} obtained from the data in Table I. It appears likely that the same change is being observed in the two experiments. The absolute values of T_1 depend rather critically upon the concentration of the paramagnetic ion in the crystal. Table I indicates that T_1^0 decreases as concentration increases.

Since $\rho(\nu)$ and $\langle n_0 \rangle$ are computable it is possible to obtain an estimate of the spin-lattice transition probability per unit of phonon excitation which should depend only on the parameters of the spin and electronic state of the ion. These estimates are shown in Table I and it appears that the concentration of ions also affects the value of A . The phonon-bath relaxation times at 4.2° K also appear to change with concentration as shown in the table; whether they are in fact independent of the paramagnetic ion concerned, remains to be seen as more crystals are examined. The results obtained are in agreement with those suggested by Strandberg (1958) of less than 10^{-5} or 10^{-6} seconds.

Attempts were made to observe saturation of the crystals at liquid air temperatures but insufficient power was available to obtain very reliable results. They did, however, indicate that T_1^0 decreases as about T^{-1} . The phonon-bath relaxation times were not determinable at these temperatures.

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REFERENCES

- BLOCH, F. 1946. *Phys. Rev.* **70**, 460.
BLOEMBERGEN, N. 1956. *Phys. Rev.* **104**, 324.
BLOEMBERGEN, N., PURCELL, E. M., and POUND, R. V. 1948. *Phys. Rev.* **73**, 679.
DAVIS, C. F., STRANDBERG, M. W. P., and KYHL, R. L. 1958. *Phys. Rev.* **111**, 1268.
ESCHENFELDER, A. H. and WEIDNER, R. T. 1953. *Phys. Rev.* **92**, 869.
FEHER, G. and SCOVIL, H. E. D. 1957. *Phys. Rev.* **105**, 760.
GIORDMAINE, J. A., ALSOP, L. E., NASH, F. R., and TOWNES, C. H. 1958. *Phys. Rev.* **109**, 302.
MEYER, J. W. 1955. M.I.T. Lincoln Lab. Report M35-46.
SCOVIL, H. E. D., FEHER, G., and SEIDEL, H. 1957. *Phys. Rev.* **105**, 762.
STRANDBERG, M. W. P. 1958. *Phys. Rev.* **110**, 65.
SWARUP, P. 1959. *Can. J. Phys.* **37**, 848.
VAN VLECK, J. H. 1940. *Phys. Rev.* **57**, 426.

NOTES

γ -RADIATION AT AIR-GROUND INTERFACES WITH DISTRIBUTED Cs^{137} SOURCES*

C. E. CLIFFORD, J. A. CARRUTHERS,[†] AND J. R. CUNNINGHAM[‡]

For problems involving the γ -ray dose due to distributed sources it is important to take account of the scattering and absorption at the air-ground interface. In recent work at the Defence Research Chemical Laboratories (Clifford *et al.* 1959) measurements have been made that show the effects of different "ground" materials on the dose at varying heights and radial distances from a γ -source on the ground. Cs^{137} was used as the source since the γ -ray energy (0.66 Mev) is close to the average energy of γ -rays from fission "fall-out".

Some of the more important results of these measurements are given and it is also of interest to compare these results with calculations by Berger (1957) for somewhat similar conditions but for a higher photon energy of 1.28 Mev, corresponding to Co^{60} γ -rays.

Figure 1 shows the results of measurements made over smooth clay earth and compares the results to Berger's Monte Carlo calculations for 1.28 Mev in

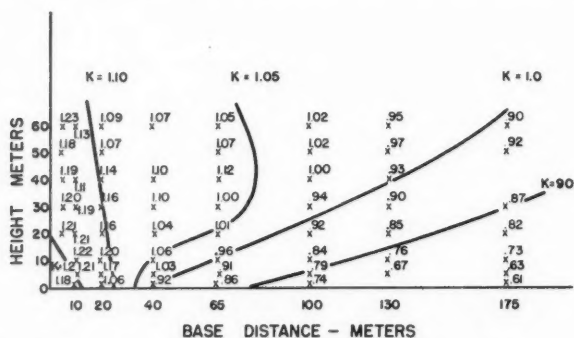


FIG. 1. Boundary correction factor K in air above smooth clay earth. \times , measured values with Cs^{137} at an air-ground interface; — from Berger's calculations for Co^{60} .

which ground and air were assumed to have the same scattering properties per unit mass as water. The parameter K which appears is the factor by which the dose is altered by the presence of the denser medium. Since both Co^{60} and Cs^{137} γ -rays are in the energy region of Compton scatter for low and medium

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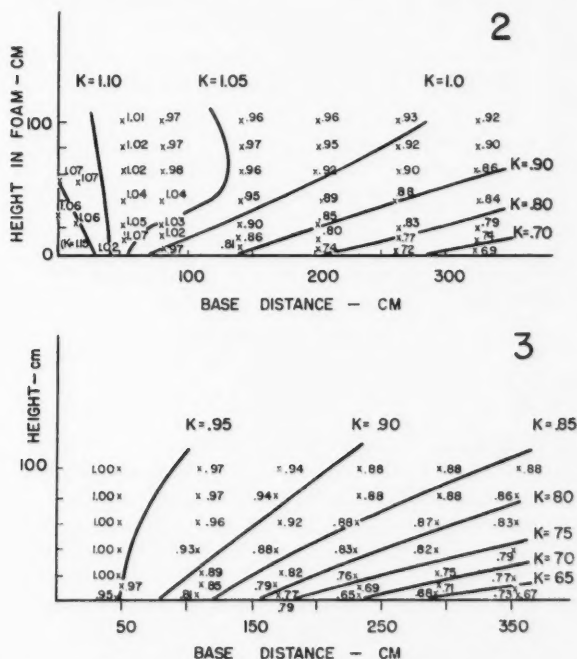
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Z materials, it might be anticipated that K values calculated for 1.28 Mev would be little changed at 0.66 Mev when distances are expressed in mean free paths. At energies below the region of predominant Compton scatter, experimental K values would be expected to vary from those calculated at higher energies. Good experimental agreement with the calculations was reported by Titus (1958) at 1.28 Mev for a Co^{60} source at the plane boundary between media of steel wool and steel. The agreement shown in Fig. 1 for the lower energy γ -rays from Cs^{137} indicates the accuracy with which Berger's values could be used in fall-out analysis.

Similar K values, obtained from measurements made in a region of polyfoam (i.e. expanded polystyrene) of density 0.072 g/cc with a Cs^{137} source located at a polyfoam-concrete boundary, are shown in Fig. 2. Here the experimental K values shown were obtained by taking the ratio of the dose measured at the indicated base distance and height to the dose observed at an equivalent distance when the source and detector were embedded in polyfoam 3½ feet above the polyfoam-concrete boundary.

Because Monte Carlo calculations were available (Berger 1957) giving K values for the limiting case of a source lying on the surface of a completely



absorbing medium, the polyfoam was used to obtain experimental values. This was done by stacking the polyfoam above a floor of lead bricks and measuring the dose at different distances and heights in the foam when a Cs^{137} source was placed on the surface between the lead and polyfoam. Since the ground is now an absorbing medium, the dose should be something less than the dose in an infinite polyfoam medium. The results are shown in Fig. 3 where the lines represent the Monte Carlo calculations for a Co^{60} source on an infinitely absorbing medium. The somewhat higher experimental K values are probably due to the use of a source of lower energy γ 's than Co^{60} and to the extent to which the lead floor is not a perfect absorber. The trend of the K values is quite similar and further illustrates the reliability of Monte Carlo calculations.

The spectra of the collimated radiation received at various angles were measured and analyzed to give the dose received through a solid angle of 0.1 steradian as a function of the direction angle of a collimated detector located 1 meter above an air-ground interface uniformly contaminated with Cs^{137} . The resulting polar distribution of radiation is shown in Fig. 4 where the doses

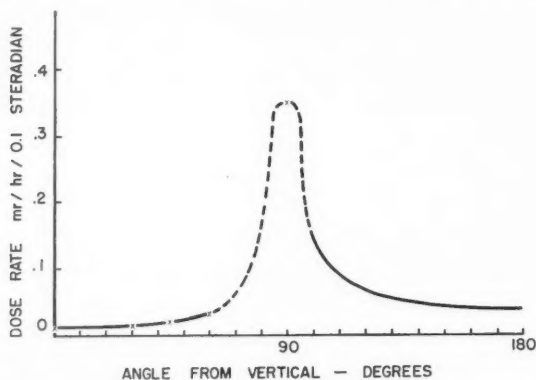


FIG. 4. Polar distribution of radiation. Dose rate per 0.1 steradian at a height of 1 meter above a plane uniformly contaminated with $1 \text{ mc Cs}^{137}/(\text{meter})^2$.

calculated from the spectra are shown as crosses. The solid line between angles of 100° and 180° measured from the vertical was calculated for primary radiation only since a detector at a height of 1 meter will see only small amounts of scattered radiation arriving in these angular limits. When integrated over the 4π steradians this polar distribution should lead to the total dose actually observed at a height of 1 meter in a uniformly contaminated field. The dotted line was chosen to satisfy this requirement. It is interesting to note that the resulting curve indicates that 73% of the total dose is due to radiation received within $\pm 20^\circ$ of the horizon. These measurements were made with contamination on a smooth plane. In the practical case of fall-out it is appreciated that the polar distribution of radiation would be modified somewhat depending on the extent of ground roughness.

- BERGER, M. J. 1957. *J. Appl. Phys.* **28**, 1502.
 CLIFFORD, C. E., CARRUTHERS, J. A., and CUNNINGHAM, J. R. 1959. Defence Research Chemical Laboratories, DRCL Report 296.
 TITUS, F. 1958. *Nuclear Sci. and Eng.* **3**, 609.

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A NOTE ON DIFFRACTION BY A HALF PLANE

W. E. WILLIAMS

INTRODUCTION

The problem of the diffraction of the field of a line source by a perfectly conducting half plane was first solved by Carslaw (1899) using a method similar to that employed by Sommerfeld (1896) in considering diffraction by a plane wave. The problem was also considered by Macdonald (1915) using a completely different approach and, in particular, he succeeded in expressing the solution in an extremely simple manner. This latter form of the solution was recently rederived by Clemmow (1950) using yet another method. Though the form of Macdonald's solution is extremely simple the methods used in obtaining it involve a considerable amount of analysis and the object of the present note is to give a simple method of solving this problem involving very little analysis. For plane-wave excitation a comparable type of simple solution has been obtained by Lamb (1906).

FORMULATION OF THE PROBLEM

A Cartesian co-ordinate system $0xyz$ is chosen so that the half plane occupies the region $y = 0$, $x \geq 0$, all z ; it is also convenient to define polar co-ordinates (r, θ) by $x = r \cos \theta$, $y = r \sin \theta$. We shall consider an electric line source parallel to the z axis and its intersection with the plane $z = 0$ will be taken to be at the point (x_0, y_0) or, in polar co-ordinates, (r_0, θ_0) . Two other geometrical quantities which will be required are the distances R_1 and R_2 of (x, y) from (x_0, y_0) and $(x_0, -y_0)$ respectively. In terms of polar co-ordinates they are defined by

$$R_1^2 = r^2 + r_0^2 - 2rr_0 \cos(\theta - \theta_0), \quad R_2^2 = r^2 + r_0^2 - 2rr_0 \cos(\theta + \theta_0).$$

The only component of the electric field will be parallel to the z axis and it will be denoted by $\phi(x, y, x_0, y_0) \exp i\omega t$. Maxwell's equations show that

$$(1) \quad (\nabla_1^2 + k^2)\phi = \delta(x - x_0)\delta(y - y_0),$$

where ∇_1^2 is the two-dimensional Laplacian operator, $\delta(x)$ is Dirac's function, and $k^2 = \omega^2 \epsilon_0 \mu_0$ where ϵ_0 , μ_0 denote the electric susceptibility and magnetic permeability (in m.k.s. units) of free space.

ϕ is finite except at (x_0, y_0) , it vanishes on the half plane, and it satisfies Sommerfeld's radiation condition at infinity. We also have that ϕ satisfies the reciprocity condition, i.e. $\phi(x, y, x_0, y_0) = \phi(x_0, y_0, x, y)$. In solving a diffraction problem it is necessary to make some assumption concerning the behavior of the solution near sharp edges of diffracting obstacles. In the present case we shall make the assumption, following Bouwkamp (1954), that ϕ behaves as $r^{\frac{1}{2}}$ near $r = 0$. All known solutions of diffraction problems involving thin sheets do, in fact, exhibit this behavior near the edge of the diffracting sheet. In fact, if it is assumed that ϕ behaves as r^{λ} near $r = 0$ then it may be shown that the smallest permissible value of λ is $\frac{1}{2}$. We shall make the assumption that, near $r = 0$, ϕ has the form $r^{\frac{1}{2}}f(\theta)$ where f is a function of θ . In order that ϕ satisfies equation 1 it is easily verified that $f = A \sin \frac{1}{2}\theta + B \cos \frac{1}{2}\theta$ where A, B are independent of r and θ . Furthermore, since $\phi = 0$ on the half plane, we have $B = 0$.

From ϕ we can construct a new function χ which also vanishes on the half plane and satisfies the radiation condition. This function is defined by $\chi = (\partial\phi/\partial x) + (\partial\phi/\partial x_0)$. From equation 1 it is seen that χ is non-singular at (x_0, y_0) and is, in fact, a solution of the homogeneous Helmholtz equation. Our assumption about the edge behavior of ϕ shows that, near $r = 0$, χ has the form $-\frac{1}{2}Ar^{-\frac{1}{2}}\sin \frac{1}{2}\theta$. Thus a possible solution for χ is $-\frac{1}{2}Ar^{-\frac{1}{2}}\sin \frac{1}{2}\theta \exp -ikr$. This solution satisfies the homogeneous Helmholtz equation, the radiation condition, the boundary condition on the half plane and possesses the appropriate edge singularity. The most general solution for χ consistent with our assumption about the edge behavior is thus obtained by adding to the above particular solution a second solution of Helmholtz' equation which is non-singular at the edge. This second solution is also to be finite everywhere and to satisfy Sommerfeld's radiation condition. The uniqueness theorem of Peters and Stoker (1954) shows that such a function is everywhere zero and hence $\chi = -\frac{1}{2}Ar^{-\frac{1}{2}}\sin \frac{1}{2}\theta \exp -ikr$. The form of χ shows that it satisfies the reciprocity condition and thus A must have the form $B \sin \frac{1}{2}\theta_0 r_0^{-\frac{1}{2}} \exp -ikr_0$ where B is a numerical constant.

The boundary value problem thus reduces to integrating the partial differential equation

$$(2) \quad \frac{\partial\phi}{\partial x} + \frac{\partial\phi}{\partial x_0} = -\frac{B \sin \frac{1}{2}\theta \sin \frac{1}{2}\theta_0}{2\sqrt{(rr_0)}} \exp -ik(r+r_0).$$

It is not immediately obvious how this equation may be integrated and the correct line of attack is obtained by considering the particular case of $k = 0$. This corresponds to determining a solution of Laplace's equation with a line charge at (r_0, θ_0) ; the solution to this problem may be obtained by conformal mapping (Jeans 1951). The solution is given as a linear combination of variables η_1 and η_2 defined by

$$\eta_1 = \sinh^{-1} \frac{2\sqrt{(rr_0)}}{R_1} \cos \frac{1}{2}(\theta - \theta_0), \quad \eta_2 = \sinh^{-1} \frac{2\sqrt{(rr_0)}}{R_2} \cos \frac{1}{2}(\theta + \theta_0).$$

The form of η_1 and η_2 suggests writing the product of sines in equation 2 as a difference of cosines and writing ϕ as $\phi_1 - \phi_2$ where

$$(3) \quad \frac{\partial \phi_1}{\partial x} + \frac{\partial \phi_1}{\partial x_0} = -\frac{B \cos \frac{1}{2}(\theta - \theta_0)}{4\sqrt{(rr_0)}} \exp -ik(r+r_0),$$

$$(4) \quad \frac{\partial \phi_2}{\partial x} + \frac{\partial \phi_2}{\partial x_0} = -\frac{B \cos \frac{1}{2}(\theta + \theta_0)}{4\sqrt{(rr_0)}} \exp -ik(r+r_0).$$

The form of the solution for $k = 0$ suggests that we choose η_1 and η_2 as new variables and it is easily verified that

$$\frac{\partial \eta_1}{\partial x} + \frac{\partial \eta_1}{\partial x_0} = \frac{\cos \frac{1}{2}(\theta + \theta_0)}{\sqrt{(rr_0)}}, \quad \frac{\partial \eta_2}{\partial x} + \frac{\partial \eta_2}{\partial x_0} = \frac{\cos \frac{1}{2}(\theta - \theta_0)}{\sqrt{(rr_0)}},$$

$$r+r_0 = R_1 \cosh \eta_1 = R_2 \cosh \eta_2.$$

The above relations indicate that ϕ_1 is a function of R_2 and η_2 and ϕ_2 a function of R_1 and η_1 . Thus, since $(\partial R_1/\partial x) + (\partial R_1/\partial x_0) = (\partial R_2/\partial x) + (\partial R_2/\partial x_0) = 0$, equations 3 and 4 may be integrated immediately to give the following particular integrals

$$\phi_1 = -\frac{1}{4}B \int_a^{\eta_2} \exp(-ikR_2 \cosh \eta) d\eta, \quad \phi_2 = -\frac{1}{4}B \int_b^{\eta_1} \exp(-ikR_1 \cosh \eta) d\eta.$$

a and b are constants to be determined. In the neighborhood of $(x_0, -y_0)$, $\eta_2 \approx -\infty$ and $R_2 \approx 0$; thus ϕ will be infinite near $(x_0, -y_0)$ unless $a = -\infty$. $R_1 = R_2$ and $\eta_1 = \eta_2$ on the half plane and thus, since $\phi = 0$ on the half plane, $b = -\infty$. Thus choosing $a = b = -\infty$ produces a solution satisfying all the conditions imposed except that at (x_0, y_0) . The behavior at the source is determined by an appropriate choice of B . If we let R_1 tend to zero in ϕ_2 then the integral representation of the Hankel function (Watson 1944) shows that, near (x_0, y_0) , $\phi_2 \approx -\frac{1}{4}B\pi i H_0^{(2)}(kR_1)$ and hence $B = 1$.

Thus the solution to the boundary value problem has been obtained by assuming the edge behavior of the solution and employing the reciprocity condition.

The above method may also be employed to determine time-dependent solutions of the wave equation. It is easily verified that the two-dimensional time-dependent Green's function is obtained when the exponential in equations 3 and 4 is replaced by

$$\delta\left\{t - \frac{1}{c}(r+r_0)\right\}$$

where c is the wave velocity. The integration of the equations is elementary and the solution obtained agrees with that given by Friedlander (1951). If the exponential is replaced by

$$u\left\{t - \frac{1}{c}(r+r_0)\right\},$$

where u is the unit function, then the solution for a cylindrical pulse is obtained. The problem for the spherical pulse, solved by Wait (1957), may also be treated in this manner. In this case the exponential is replaced by

$$\frac{4\pi^2 t(r+r_0)}{\{z^2 + (r+r_0)^2\}^{\frac{1}{2}} \left\{ t^2 - \frac{1}{c^2} [z^2 + (r+r_0)^2] \right\}^{\frac{1}{2}}} u \left\{ t - \frac{1}{c} [z^2 + (r+r_0)^2]^{\frac{1}{2}} \right\}.$$

The solution for a time harmonic point source is also easily obtained by the present approach.

- BOUWKAMP, C. J. 1954. Repts. Progr. in Phys. **17**, 38.
 CARSLAW, H. S. 1899. Proc. London Math. Soc. **30**, 121.
 CLEMMOW, P. C. 1950. Quart. Jour. Mech. Appl. Math. **3**, 377.
 FRIEDLANDER, F. G. 1951. Quart. Jour. Mech. Appl. Math. **4**, 344.
 JEANS, J. H. 1951. Electricity and magnetism (Cambridge University Press), p. 283.
 LAMB, H. 1906. Proc. London Math. Soc. **4**, 190.
 MACDONALD, H. M. 1915. Proc. London Math. Soc. **14**, 410.
 PETERS, A. S. and STOKER, J. 1954. J. Commun. Pure Appl. Math. **7**, 565.
 SOMMERFELD, A. 1896. Math. Ann. **47**, 317.
 WAIT, J. R. 1957. Can. J. Phys. **35**, 693.
 WATSON, G. N. 1944. Theory of Bessel functions (Cambridge University Press), p. 170.

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FRANCK-CONDON FACTORS AND r -CENTROIDS FOR SOME BANDS OF THE CO FOURTH POSITIVE ($A''\Pi-X'\Sigma$) BAND SYSTEM

W. R. JARMAIN, RUBY EBISUZAKI,* AND R. W. NICHOLLS†

The Franck-Condon factor $q_{v',v''}$ arrays of a number of band systems of combustion interest discussed by Gaydon (1957) were recently published (Nicholls, Fraser, and Jarman 1959). The extent of each of the arrays was limited to include only bands which were in the readily accessible wavelength region (2000 Å to 10,000 Å) of standard photographic spectroscopy, and whose $q_{v',v''}$ values were amenable to computation, by desk calculator or electronic computer, using the methods of Fraser and Jarman (Fraser and Jarman 1953; Jarman and Fraser 1953; Fraser 1954) for Morse molecules. The fact that the bands of the CO fourth positive system (which as a whole extends in wavelength between about 1000 Å and 2800 Å), at longer wavelengths than 2000 Å, arise from transitions between high vibrational levels, precluded the use of the Fraser-Jarman method for these bands although they are of combustion interest.

A partial Franck-Condon factor array ($v' + v'' \leq 7$) was, however, computed some years ago for this system as part of a routine program of such

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calculations. It gives data for bands whose wavelengths are less than 1988 Å. The recent growth in interest in intensity aspects of vacuum ultraviolet spectra together with private requests for the array prompts us to present it in Table I together with band head wavelengths and r -centroids. The wave-

TABLE I

Franck-Condon factors $q_{v'v''}$, r -centroids $\bar{r}_{v'v''}$, and wavelengths $\lambda_{v'v''}$ for the CO fourth band system

$v' \backslash v''$	0	1	2	3	4	5	6	7
0	0.11 ₄ 1.181 1545.3	0.26 ₁ 1.211 1597.14	0.28 ₆ 1.241 1653.05	0.19 ₄ 1.271 1712.19	0.09 ₆ 1.302 1774.90	0.03 ₃ 1.334 1841.47	0.01 ₀ 1.366 1912.8	(0.00 ₂)‡ 1.398 1988.08†
1	0.21 ₆ 1.160 1509.66	0.15 ₄ 1.190 1560.14*	0.00 ₂ 1.220 1613.99†	0.05 ₉ 1.248 1669.68	0.19 ₄ 1.280 1729.25	0.18 ₄ 1.311 1792.38	(0.09 ₄) 1.342 1859.3	
2	0.23 ₀ 1.141 1477.48	0.01 ₂ 1.170 1525.75	0.09 ₁ 1.200 1576.67	0.11 ₄ 1.223 1630.40	0.00 ₆ 1.259 1687.44†	(0.07 ₅) 1.289 1747.20		
3	0.18 ₄ 1.123 1447.27	0.02 ₆ 1.151 1493.60	0.11 ₄ 1.179 1542.34	0.00 ₆ 1.209 1593.97†	(0.10 ₄) 1.238 1647.90			
4	0.11 ₉ 1.105 1418.91	0.08 ₄ 1.133 1463.47*	0.03 ₄ 1.161 1510.47†	(0.07 ₄) 1.189 1559.47				
5	0.069 1.088 1391.97	0.12 ₄ 1.115 1435.28	(0.00 ₆) 1.143 1480.43†					
6	0.03 ₇ 1.072 1367.70†	(0.11 ₄) 1.099 1408.8						
7	(0.01 ₄) 1.057 1344.27†							

LEGEND:

 $q_{v'v''}$ $\bar{r}_{v'v''}$ (Å) $\lambda_{v'v''}$ (Å)

*Bands observed overlapped, wavelengths thus calculated, not measured, by Read (1934).

†Bands not reported, wavelengths calculated.

‡Franck-Condon factors in parentheses not perturbation corrected.

lengths were taken from the work of Headrick and Fox (1930) and of Read (1934). The r -centroids were evaluated graphically by methods described by Nicholls and Jarman (1956), and the Franck-Condon factors were evaluated by the method of Fraser and Jarman (including perturbation correction) using the basic data for the transition tabulated by Herzberg (1950).

As expected for a band system which involves a moderately large change in internuclear separation ($\Delta r_e = 0.107$ Å), the primary Condon "Parabola" of the $q_{v'v''}$ values is fairly wide and does not quite include the (0,0) band. There is also evidence of a secondary parabola whose vertex is in the region

of the (2,2), (2,3), and (3,2) bands. Some recent studies by one of us on the analytical form of the Condon "Parabola" in cases where the potentials involved are not parabolic will be published shortly. A much more extensive r -centroid array for the CO fourth positive system than that presented in Table I is available as part of a comprehensive compilation of such data for a wide variety of band systems, and is in the process of publication elsewhere.

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- FRASER, P. A. 1954. *Proc. Phys. Soc. A*, **67**, 939.
FRASER, P. A. and JARMAN, W. R. 1953. *Proc. Phys. Soc. A*, **66**, 1145.
GAYDON, A. G. 1957. *The spectroscopy of flames* (Chapman & Hall Ltd., London).
HEADRICK, L. B. and FOX, G. W. 1930. *Phys. Rev.* **35**, 1033.
HERZBERG, G. 1950. *The spectra of diatomic molecules* (D. Van Nostrand Company, Inc., New York).
JARMAN, W. R. and FRASER, P. A. 1953. *Proc. Phys. Soc. A*, **66**, 1153.
NICHOLLS, R. W. and JARMAN, W. R. 1956. *Proc. Phys. Soc.* **69**, 253.
NICHOLLS, R. W., FRASER, P. A., and JARMAN, W. R. 1959. *Combustion and Flame*, **3**, 11.
PEARSE, R. W. B. and GAYDON, A. G. 1950. *The identifications of molecular spectra*, 2nd ed. (Chapman & Hall, Ltd., London).
READ, D. N. 1934. *Phys. Rev.* **46**, 571.

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LETTERS TO THE EDITOR

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Frequency Measurement of Standard Frequency Transmissions¹

Measurements are made at Ottawa, Canada, using N.R.C. caesium-beam frequency resonator as reference standard (with an assumed frequency of 9 192 631 770 c.p.s.). Frequency deviations from nominal are quoted in parts per 10¹⁰. A negative sign indicates that the frequency is below nominal.

Date, December 1959	MSF, 60 kc/s	GBR, 16 kc/s			KK2XE1, 60 kc/s
		8½-hour average*	24-hour average		
1	-159	-164	-161		-82
2	N.M.	-166	-166		-81
3	N.M.	-164	-167		-80
4	N.M.	-163	-166		-81
5	N.M.	-169	N.M.		N.M.
6	N.M.	N.M.	N.M.		N.M.
7	N.M.	N.M.	N.M.		N.M.
8	-163	N.M.	N.M.		-78
9	N.M.	-164	-162		N.M.
10	-166	-160	-162		-79
11	-165	-165	-164		-82
12	-163	-164	-162		N.M.
13	-173	-164	-164		N.M.
14	-170	-160	-161		-79
15	-172	-161	-163		-78
16	-158	-160	-161		-76
17	-162	-163	-161		-78
18	-163	-161	-161		-78
19	-165	-163	-162		N.M.
20	-165	-162	N.M.		N.M.
21	N.M.	-160	-161		-80
22	N.M.	-162	-162		-79
23	N.M.	-160	-161		-77
24	N.M.	-164	-163		-78
25	-171	-164	-164		N.M.
26	N.M.	-163	-164		N.M.
27	-166	-166	-163		N.M.
28	-155	-161	-162		-76
29	-163	-164	-161		-78
30	-156	-161	-157		-74
31	-162	-163	-162		-73
Midmonthly mean	-164	-163	-163		-78
Midmonthly mean of WWV	-106				

NOTE: N.M. no measurement.

*Time of observations: 00.00 to 07.00 and 22.30 to 24.00 U.T.

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²Cf. Kalra, S. N. 1959. Can. J. Phys. 37, 1328.

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Canadian Journal of Physics

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